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LXVIII. *An Analysis of the Spectrum of Hg II.*

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THE present paper was very largely written up when, by the kindness of Dr. Paschen, the author became acquainted with his communication to the Berlin Academy † in which he had discussed the Hg ii spectrum on the basis of a new set of observations on the spectrum produced by his method of the hollow cathode, which is peculiarly suitable for this purpose. Our two results are quite different, but not mutually exclusive (saving a few allocations) except in one crucial point. While we have both taken the accepted 35104 as S_1^{22} , we have given to the p_{12} term in this values differing by 1363. Both cannot be correct, unless we accept the incredible supposition that the same frequency can be caused by transitions between different pairs of levels. Paschen's allocations march well with those for Zn ii and Cd ii given by von Salis ‡, and at a first glance seem to hold well together. At the same time those of my discussion seemed to me also to hold together, and they had led to the recognition of a new class of facts, possible but only occurring in rich spectra, indeed explaining to some extent why a spectrum like that of mercury is so rich in lines. A special examination of Paschen's

* Communicated by the Author.

† *Sitz. Ber. preuss. Akad.* 32, 1, 28.

‡ *Ann. der Phys.* 76, 145, 25.

results therefore seemed called for, with special reference to the contradiction above referred to. The result has been to lead me to the conviction that the line $n=35104$ does not belong to his $S(2.m)$ system. I give the result of my discussion as Part II. of this paper. The natural procedure would have been to make it Part I., but many points of the argument could not have been followed without a previous knowledge of the result of my own analysis. It is needless to say that the general arrangement of his allocations (Pm excepted) is little affected.

My analysis has shown that the lowest p_2^* level is multiple. In other words, that to one $P_1(m)$, $S_1(2.m)$, $D_1(2.m)$ several P_2 , S_2 , D_2 lines appear. It has not been possible to decide whether there is one particular p_2 , with, so to say, accidentals, or whether there are a definite number of equal normality. That must be left for a more complete analysis than is possible in a preliminary paper. But the more probably occupied p_2 levels appear to be restricted to four. The result of this multiplicity is to produce a number of different doublet separations. As the d terms depend ultimately on the lowest d_2 term, which itself is determinable in terms of these p displacements, it would follow that if the various p_2 were equally normal, we should find a corresponding number of independent D series. I have made a preliminary test for these, and believe I have found definite evidence for their existence; but it will be sufficient here to give the evidence for one only, with corresponding F and G series. The general argument is given in the text, but the details, many of very great interest, are given in the notes to the different series tables.

The mercury spectrum shows evidence of the presence of the satelloidal effect, although it is not so striking and conclusive as in copper. The evidence is given in § 8, which may be read, perhaps with advantage, before the general discussion.

* Throughout, Rydberg's notation is used. This is based directly on observed relations, as all notations should be. To base a general notation on a theory current at a special instant seems subject to two serious objections: (1) a constant change with theory most exasperating to future readers; (2) it lays too much stress on the correspondence of the last-made hypothesis to reality. As a fact, although not so originally intended, Rydberg's subscripts may be regarded as giving the order in which the different levels—such as p_1 , p_2 , p_3 —are met with as we pass from outside into the nucleus.

I have recently † suggested that when the energy of a transition has been transmitted to the nucleus, the latter would emit it as a radiation of frequency given by $E = nh\nu$, in which n is not restricted to unity, as is usually supposed. I had originally intended to merely illustrate this by giving such examples as might have been noted in Hg II as a mere list of raw material for future consideration. But so many were found, and they threw so much light on the cause of the non-appearance of certain lines, especially in S_1m , that I have discussed them in the notes to the various series as they arose. A * is attached to each line showing this effect. They are collected also in a single table at the end of Part I.

PART I.

References are concisely referred to by three successive numbers. Thus 21, 105, 28 denote vol. 21, p. 105, year 1928.

W.N.=wave number. O.E.=observation error. O-C $d\lambda$ means excess of observed wave-length over a calculated value.

Unless expressly noted, λ or n to three decimal places are by Stiles, and in *R.A.*, given in italics, by Eder and Valenta; also below $\lambda=1760$ by Carroll. E. V.=Eder and Valenta. E. H.=Exner and Haschek. K. R.=Kayser and Runge. Stk.=Stark. Ly.=Lyman. S.=Stiles. Bl.=L. and E. Bloch. D.=Déjardin. Cd.=Cardaun. C.=Carroll. P.=Paschen. McL.=McLennan. W.=Wiedmann.

Series lines p_2-sm , p_3-sm , etc., are written $S(2.m)$, $S(3.m)$, etc. Shifts produced in a term by a one-oun displacement are indicated by a thick minus. Thus p_12- is change in the value of p_12 by one oun.

1. The elements of group II. show very close correlation between the corresponding series lines in the neutral and singly ionized spectra. This fact is of considerable assistance in arriving at the constitution of the unknown Hg II series. In particular we find—

1. In all cases the first separation of the doublet is a little less than twice the first separation of the triplet.
2. The denominators of p_1^{31} and p_1^{22} in each sub-group are very closely in the same ratio ‡.

In the Zn-subgroup these ratios for doublet and triplet for Zn, Cd, Eu are 1.312, 1.306, 1.32. For Hg we should then expect a ratio close to 1.32. The first separation of

† "The Nucleus as Radiator," Phil. Mag. 8, 108, 29.

‡ Phil. Mag. 44, 351, 22.

the triplet in neutral Hg is $\nu_1 = 4630.6$. We expect then a doublet separation a little less than 9261. The denominator of $p_1^3 1$, or 40141 is 1.65296. This multiplied by 1.32 should then be of the order of the denominator of $p_1^2 2$. The result, $4R/(2.1819)^2 = 92156$, should then be within a few hundreds of the true $p_1^2 2$, *i.e.*, the limit of the S_1^2 series.

In his memoir of 1890, Rydberg suggested as analogues of the doublets he had found in Zn and Cd the lines (W.N. in modern measures)

2,	35104.16	9829.28	44933.4
3,	39412.27	---	---

The 39412 is now known to be a definite neutral line, but the first set have ever since been accepted as the representatives of $S^2 2$. Indeed, we can take 35104 quite definitely as $S_1^2 2$, for not only is it in complete step with that of the other elements, but Runge* and Paschen have found a Zeeman pattern for it supporting this allocation. Many other instances of the 9829 separation occur in the spectrum; but although the observed region has since been much extended, no one has yet succeeded in arranging other pairs in S or D series. Carroll, who has pushed the observed region down to $\lambda = 740$, has proposed certain allocations. He says that he had been unable to make any progress on that basis. When writing my critical studies of spectra many years ago, I came to the same conclusion, and tried, in place of it, another very common separation of 9333 which also is much closer to the expected value, but again in vain. Carroll has used another separation value of 9122, also very common.

Let us start from the given datum of $S_1^2 = 35104$, and examine the spectral data at about 9260 ahead. We find a bunch of very strong lines in Déjardin's Class E_1 . They are reproduced here with some weaker ones for later use. The measures of Cardaun are used where available. The separations from 35104 are given in thick type, followed by ordinal numbers for reference. Of the numbers following the W.N., the first gives the intensity according to Déjardin, the second according to Cardaun, and the third, in roman numerals, gives Déjardin's

* Astro. J. 15, 233, 02.

classification E_1 . . . according to the increasing intensity of the excitation at which they first appear.

69	9051.17	1	44155.33	0	- iii?	λ 2264.03	
	56.44	2	160.60	5, 2 <i>n</i>	i	63.76	
69 $\frac{1}{4}$	86.59	3	190.75	7, 3, i		62.215	
67 $\frac{1}{2}$	9121.88	4	226.04	7, 3 <i>n</i>	i	60.41	
	9268.89	5	373.05	7, 3 <i>n</i>	i	52.92	
71	9333.41 ⁽¹⁾	6	- - -				
35104.16 10 <i>n</i> , 8 <i>n</i> , i	71 $\frac{1}{4}$	71.94	7	476.10	2 <i>n</i> - i	47.70	
	71 $\frac{3}{4}$	9438.72	8	542.88	7 - ii	44.33	
	72 $\frac{1}{4}$	9507.08	9	611.24	0 <i>n</i> - i	40.89	
	72 $\frac{3}{4}$	80.6	10	684.8	0 - i?	37.2	
	73 $\frac{1}{4}$	9724.11	11	828.27	5 - i	30.04	
	74	57.91	12	862.07	1 - ii	28.36	
	74 $\frac{1}{2}$	9829.28	13	933.44	10, 3 <i>n</i>	i	24.82
	75	9903.31	14	45000.6	0 - i	21.5	

(¹) This separation has not been observed from 35104. But it is here inserted as it will be found to be one of the most important in the series relations. No. 4 shows it back, thus 34892.26 **9333.78** 44226.04.

Confine attention first to the lines observed by Cardaun, shown in italics. They are all of the same character, and there is nothing to show which is definitely S_22 , except that the separation 9829 leads to a line which Déjardin shows as much more intense than the others. Can it be that they all belong to S_22 ? In other words, are there a set of independent p_2 terms? If so, since all separations depend on multiple oun displacements, they must all be collaterals of one another. Now if we compare the separations to Déjardin's strong lines, but taking 1 in place of 2, omitting 5, and including 9333, their successive differences are 35, 35, 211, 105, 286, 105. All these are multiples of 35, again strongly suggesting displacement. This can roughly be tested at once, since the value of p_1 is known so closely, and p_2 should be about 9300 ahead, or equal to about 101400. A rough calculation shows that one-oun displacement shifts 30.5 in p_1 and 35.5 in p_2 . Now it is quite easy to find such a value of p_1 , near 92156, that a suitable multiple oun displacement will produce a separation of given value, say 9086.59. But it will not produce all the others correctly unless they are actually such a set of mutual collaterals. As a fact we do find this.

We get such a set by taking $p_1=92024\cdot56$. To allow for O.E. in the separations take this $+\xi$ as the true p_1 . Then

$$p_1^2=92024\cdot56+\xi=4R/\{2\cdot183432-11\cdot863\xi\}^2.$$

$$\text{Ratio } p^2, p^3 \text{ denominators}=1\cdot321.$$

$$\text{also } \delta=1450\cdot090 * \pm 0\cdot009, \delta_1=362\cdot522,$$

The separations as calculated are as follows, the own multiple displacements being written on the right in terms of δ and the observed values below with $O-C \, d\lambda$ in ().

- | | | |
|---|--|--|
| 1. 9051·41 $+150\xi$, 69
51·17 ($-0\cdot01$) | 6. 9333·41 $+155\xi$, β
29·28 ($0\cdot023$) | 13. 9829·74 $+164\xi$, γ
70½ |
| 3. 9086·59 $+152\xi$, 69½
86·59 (0) | 8. 9439·45 $+158\xi$, 71½
(38·72) ($0\cdot03$) | (5) 9262·80 $+155\xi$, 70½ |
| 4. 9121·80 $+154\xi$, α
21·88 ($0\cdot004$) | 11. 9723·08 $+162\xi$, 73½
24·11 ($-0\cdot05$) | |

The deductions according to the above method are exact within about $\cdot02$, and if the supposition is real, the values obtained must agree with the observed separations within their O.E. Any error in S_1^2 will affect all the separations by the same amount, and can be met by a suitable value of ξ . Of the others, five are by Cardaun, with small possible errors. Taking his estimates, the O.E. in W. N. may be of the order $\cdot2$ in (2), $\cdot13$ in (3), $\cdot39$ in (4), $\cdot39$ in (5), $\cdot40$ in (13). Lines (8), (11) are by E. H., and should be subject to errors of about ± 2 . It is thus seen that 9086·59 is by far the most reliable. All the separations are within their respective O.E., but the 9829 is closer to the maximum error than to be expected. It is $\cdot46$ larger, and can be explained later by a satelloid effect $y=45$, but Paschen's two readings give 9829·50 ($d\lambda=0\cdot01$). If, then, the lines involved are what they appear, viz., displaced S_2 , the limit p_1^2 can only differ from 92024·56 by a very small amount depending only on the O.E. in $S_1=35104$. This makes

$$s_2=p_1^2-S_1^2=56920\cdot18=4R/\{2\cdot776246\}^2,$$

giving a value of the denominator in close march with

* The value given in my 'Analysis' was $1450\cdot180 \pm 100$. The above has been redetermined from recent more accurate measures.

those of the other elements of this group. A further scrutiny of the lines in the S_2 region shows the existence of other separations to weak lines satisfying similar displacement conditions within O.E. They are Nos. 7, 9, 10, 12, 14 in the list above, due respectively to displacements of $71\frac{1}{4}$, $72\frac{1}{2}$, $72\frac{3}{4}$, 74, 75 δ .

Nos. 2, 5 do not conform, although they would appear to belong to the system. The relation of 2 to 1 appears to be of a "satelloidal" nature, and is discussed under that head in § 8. No. 5 *may* be of a similar nature, but another possible explanation, which would remove the line 44373 from any connexion with the S series, should not be omitted here. In a linkage map containing 35104 we find the mesh:

35104.16	9268.88	44373.02
9121.88		9121.5
44226.04	9268.5	53494.5 (1.y.)

This means that either 9121, 9268 act as links *or* we have to deal with a new term t with lines p_1-s_2 , p_2-s_2 , p_1-t , p_2-t . In this case it is easily seen that $t=47649.34=4 \times 11912.13$, whilst Rydberg's table shows that 11912 is due to a denominator 3.033. As we shall see later that these various separations do as a fact enter also as b -links, also that the separation 9262 has a considerable occurrence, and as the character of 44373 is the same as that of the other S_2 lines, we shall assume provisionally that it is actually related to the S series. The question of the reality of the relationship may at present be left open, as it has little bearing on the general dependence of the p_2 on several independent displacements in p_1 .

The question however arises, is there one normal p_2 with a normal Δ depending on a definite own multiple, the others being merely collaterals of this, *or* are some or all independent and different p_2 ? The question does not affect their values, and actually they are quantitatively collaterals. But it has important bearings on the properties of other terms—especially the d —and on the numbers of the p -links a , b , c , d , e . If there is one normal p_2 we should expect one set of p -links and one set of d terms (or at most two). If they are all independent, we should expect sets of p -links for each and corresponding d sets for each, with consequent great complexity.

We shall, however, not discuss these general links in this paper, and shall postpone the other case until we deal with the D series later.

Granting the real existence of these various p_2 levels, one important inference can be drawn. A reference to the intensities given in the list shows that those of the different S_2 are comparable with that of S_1 , that is, that the total intensities of all the S_2 lines together must very largely exceed that of S_1 . In other words, the occupancy by an electron of the outer p_12 level must have a much smaller probability than the occupancy of the lower congery of p_22 . We shall get some evidence later, however, to indicate that this is only apparently so, and is due to the energy of fall in any case being radiated according to the law $E=2h\nu$ or $3h\nu$ instead of $h\nu$. Indeed the majority of the S_1 lines show this effect.

Having definitely settled the S_12 line and the various S_2 , the next step in the analysis of the spectrum is to examine it systematically for the existence of the p separations. This has been done for 9121, 9333, 9829, or α, β, γ . The result is to show the presence of an overwhelmingly large number throughout the whole spectrum, and especially to show that, besides entering as doublet separations of S and D lines, they occur also as links. This is shown by the existence of sequences of links. Moreover, the unexpected result definitely appears that these ionized links are attached to neutral lines as well as to ionized ones. It is sufficient to mention this here, the evidence is given below (§ 9). But it is important to state one result. If p_1 receives an oun displacement, a given Δ induces the same displacement in p_2 , but the shifts produced are different, and the corresponding doublet separation is changed. If in any case these changed separations occur—especially if several are present—it is clear evidence that the p has been subject to the corresponding displacement (see, *e. g.*, notes to S1). The values are found at once from the difference between the oun shift on p_1 which is 30.557 and those on p_2 . The latter can be determined from Table I., where differences of successive p_2 give the oun shift. The change in separation in all cases is of the order 5.

2. The mantissa for $m=3$ must be slightly larger than for $m=2$, and produce a pair with a doublet separation. The only line satisfying this condition in Carroll's list, and

associated with doublet separations, is $n=61580$. Adopting this as $S_1 3$, we calculate from it and $S_1 2$ the formula

$$sm = 4R / \{m + .835827 - .119166/m\}^2.$$

The combination $s2 - s3 = 26473.90$ is observed at

$$1, 26473.742; 3776.259 \text{ A.U.}$$

Extrapolating for $m=1$ we should expect a mantissa somewhat smaller than the calculated value, which gives $S_1 1 = -54700 \pm$. We find near two sets of strong lines which are equivalent to $(\pm \delta_1)S_1(\pm \delta_1)$ requiring $S_1 = -57495.30$. Although this has been wholly disrupted, there are two for S_2 with separations respectively of 9121, 9722 ($\alpha, 73\frac{3}{4}\delta$) within O.E. (see specially the notes to S_1). Although this line is not directly observed in $h\nu$ emission, it is very exactly so in $3h\nu$ and possibly $2h\nu$. Also the corresponding $S(3.1) = -P(1.3)$ is seen, as well as a line linked to it by the e neutral link, and the combination $s1 - s2$. Thus

$\frac{1}{2} \times 57495.30 = 19165.10$	obs. 1 i	19165.044
possibly $\frac{1}{2} \times \dots = 28747.65$	obs. 1,	28745.11 W. $d\lambda = .3$
$-57495.30 + 20612.06 (=e) = 36883.24$	obs. 1 i	36883.271
$s1 - s2 = 92590.46$	obs. 4,	92584.+, $d\lambda = .16$ on 1080.1

Against this choice of S_1 it may be objected that it is out of step with the march of the corresponding series in Zn, Cd, Eu, although its mantissa is roughly in step. But no other seems acceptable. Carroll has allocated $-60609.79120.6 - 51489.06$, which at first sight seems admissible. But it is still more out of step, and, moreover, they seem quite possibly linked in series with the neutral line D_{22}^{35} (see Ex. I. in § 9). Also the intensities are in the ratio 30:50 instead of the normal ratio of 2:1. A. T. Williams ('Nature,' 124, 985, 29) states that 51489 is the true "raie ultime" and not 54063, usually taken as $S'1$.

In addition to the series $p2 - sm = S(2.m)$ we find also corresponding $p3 - sm = S(3.m)$ and $p4 - sm = S(4.m)$. We shall see later that $P_1 3$ is 14116.93, so that $S(3.m)$ must be a parallel series at a distance $-14116.93 - 35104.16 = -49221.09$. In all these sets the S_1 exhibit collaterals, often symmetrical, i. e., \pm the same displacement, whilst there are numerous observed lines for different S_2 . Indeed, in several cases the collateral displacements in the same

order in the three series are similar (see notes to Table III.). Whilst direct observations in $S_1(2.m)$ are wanting for $m=4$ and beyond, the corresponding are observed in $S_1(3.m)$ for $m=4, 9, 10, 11$ and in $S_1(4.m)$ for $m=11$. Also 5, 6, 7, 8 are disrupted into observed lines. For more complete discussion see the lists of S series below and the notes appended thereto, which will repay careful attention.

The apparent instability of the S_1 lines may be illustrated thus. Consider an electron in an outer s orbit, say above s_3 . Of those falling into the lowest p level (p_2) they either all avoid the p_1 and take, instead of p_1 , displaced p_1 orbits, or the energy of transition is emitted as $2h\nu$ or $3h\nu$. Of those falling into the p_3 levels, some may stop in p_{13} , but a large number choose displaced p_{13} . When, however, the outer s orbit is further out, the chance of falling to the p_{13} is larger, *i.e.*, the line is observed. In the great majority of cases an electron must have originally occupied a displaced s orbit when it falls into a displaced p_1 , and in several the displacement in each orbit is the same*.

As a further test of the correct allocations in S_1 and also as a test for the presence of neutral links to ionized lines, the $e.S(2.m)$ have been investigated. The neutral e link is 20612.06. The result is given in Table IV. which shows a parallel set to $S_2.2$, repeating its general features, with satelloid indications to be expected in linkages.

3. In the discussion of the data for the various S_2 lines separations due to all possible displacements between 69 δ and 75 δ were sought for (for the actual values of ν see Table I.). The result is to show that the actual p_{22} are restricted to a few only. The number of occurrences in the $S_2(2.m)$ are as follows:—

69.	$\frac{1}{4}$.	$\frac{1}{2}$.	$\frac{3}{4}$.	70.	$\frac{1}{4}$.	$\frac{1}{2}$.	$\frac{3}{4}$.	71.	$\frac{1}{4}$.	$\frac{1}{2}$.	$\frac{3}{4}$.	72.
2	3	6	2	0	1	1	1	1	1	1?	2	0
72 $\frac{1}{2}$.	$\frac{1}{2}$.	$\frac{3}{4}$.	73.	$\frac{1}{4}$.	$\frac{1}{2}$.	$\frac{3}{4}$.	74.	$\frac{1}{4}$.	$\frac{1}{2}$.	$\frac{3}{4}$.	75.	
2	0	4	0	1	0	5	1	1	5	0	1?	

* If we adopt the view as to the source of emission given in a recent paper (Phil. Mag. 8, 108, 29) we are led to the conclusion that the configuration of the nucleus of heavy atoms like Hg is not a constant one, and that each modification causes resonance at slightly different frequencies.

Some of the examples may be coincidences, but the numeration quite definitely points to four p_2 with separations due to $69\frac{1}{2}(\alpha)$, $72\frac{3}{4}$, $73\frac{3}{4}$, $74\frac{1}{2}(\gamma)$ as being, if the expression may be used, more normal than the others. In other words, the probabilities of these four levels being occupied are about equal, and much greater than that for the others. With rising orders of pm the displacements decrease in all this group, and this is indicated in Hg by a consideration of those observed in $S(3.m)$, $S(4.m)$ and $P(m)$, which, besides showing a general drift to lower multiples, also include examples between $68\frac{3}{4}$ to 67. It was not until writing up the paper that this effect was noted. A further search for lower multiples in $S(3.m)$, $S(4.m)$, and (Pm) for $m > 3$ is desirable.

The P^2 Series.

4. The true P series $s1 - pm$ will lie in the far ultra-violet, $m=2$ excepted, but we should expect also to find representatives of $s2 - pm$, where $s2 = p_12 - S_12 = 56920.18$. We start with $p_12 = 92024.56 = 4R / \{2.183432\}^2$. For p_13 we expect a mantissa somewhat greater. The nearest possible line is at 14116.93, which requires $p_13 = 42803.25$ and denominator 3.201495. Since $s1 = 149519.64$, the $P(1.m)$ series is $149519.64 - 56920.18 = 92599.46$ ahead of $P(2.m)$. The corresponding $P_1(1.3)$ should therefore be at 106716.10, and we find it at 106712 ± 5 , the ± 5 referring to equally probable values without O.E. As we shall see immediately, P_2 lines are also observed. This agreement therefore not only supports the allocation of 14116, but also the allocation for S_1 , with its value for $s1$.

The p_23 separations will depend on displacements of the same order of magnitude as those of p_2 , and we should expect to find here also the same kind of instability in the p_23 term as in p_22 , extending even, in analogy with the other elements of the group, to lower own multiples with increasing order. The values have been calculated both for p_3 and p_4 , and are given in Table I. A reference to Table V. will show that we get three representatives of $P_2(1.3)$ in the ultra-violet and four of $P_2(2.3)$ in the red, the latter by McLennan and Shover, only measured to 1 A.U.

Since for $m=4$ the mantissa is slightly larger than in $m=3$, the line 32169 fits in for P_14 . With this we get a

line for P_24 , whose measures by Stiles and by Cardaun differ by $dn=2.40$ (? satelloid effect). Their mean is separated 1196.48 from P_1 , whilst $67\frac{3}{4}\delta$ shifts 1196.86, the same within O.E., and corresponding to an equal one in P_3 . No corresponding $P(1.4)$ at 124768 is seen. These two allocations for $m=3, 4$ give the series formula. The series are also supported by indications of the parallel $P(3 . m)$ for $m=6, 7, 8$ and also by $p-p$ combinations.

The D² Series.

5. Any predetermination of the D series must depend on the fact that the mantissa of the extreme satellite term of lowest order is an exact multiple of Δ , i. e., of the displacement which produces the p doublet. To apply this rule with exactness requires a knowledge of the exact values of the D-limit (p_1), of R , and of Δ . The whole question is discussed in some detail in Chap. IX of my 'Analysis of Spectra.' It is sufficient here to say that with a good p_1^2 and Δ , as we have in the present case, and using the incorrect * $R=109678.6$ (Rydberg's value in I.A), the mantissa thus found is, as a rule, for neutral doublets at least, less than an exact multiple by a small quantity of the order 100.

In our present discussion we have the complication of the existence of a set of values of Δ , without any indication as to which is the normal one, if a single normal one really exists. Judging from the intensities of the S_2^2 lines, the Δ producing γ or 9829 would appear the normal one; judging from the rule that the doublet separation is always close to $2v_1$ of the preceding triplet series, that producing α or 9122 would appear the normal. On the other hand it is possible that several act as independent normal Δ , producing independent D and F series. If so, we shall find in the spectrum a large number of terms whose denominators differ by our multiples, and it may be

* In all data requiring the use of R , I have used this value, so as to get a uniform system between data for elements obtained at varying dates. The uniformity is necessary when dealing with displacements, and the slight difference from its true value has no appreciable effect on the results. The verification of the multiple Δ law for the extreme D satellite requires, however, for its exactness the use of the true R , which are slightly different for p and d terms. The error in W. N. at most only amounts to a few units, and is immaterial for the present purpose of identification of observed lines.

difficult in all cases to determine to which system of Δ or of d_1, d_2 terms they are to be ascribed. We should then make tests with the three α, β, γ values in succession. This has been done with some interesting results. It will be sufficient here to confine the discussion to the case of α only.

A glance at the data for the other elements of this group will show that we must expect a lowest order of $m=1$, a mantissa of about $\cdot 8$ with a satellite displacement of about $9\frac{1}{2}\delta$. Accepting this, and applying the above rules, we expect for $d_2 1$ a denominator $1+8\Delta$, and a displacement for d_1 of about $9\frac{1}{2}\delta=13776$. Here, putting in decimal points,

$$8\Delta = \cdot 806250, \quad 8\Delta + 9\frac{1}{2}\delta = \cdot 820026.$$

Calculation then at once produces $D_{12}1$, and $D_{11}1$ at lines precisely observed in the spectrum. They are:

$$8ii - 42463\cdot 90 \quad 2028\cdot 12 \quad 2i - 40435\cdot 78$$

(we anticipate by stating that corresponding F with $d-d$ combinations are also found). The denominators of these lines are

$$D_{12} \quad 1\cdot 806130 = 1 + 8\Delta - 120 \\ \cdot 013774 = 9\frac{1}{2}\delta - 2.$$

$$D_{11} \quad 1\cdot 819904$$

For the corresponding D_{22} lines see Table VI. The only peculiarity is the large intensity of the D_{12} and its class E2. This may be due to the fact that the D1 are negative lines, so that the transition is not from d to $p2$, but $p2$ to $d1$, in which the electron from $p2$ would have its more probable final level in $s1$ rather than in $d1$.

The $D_{11}2$ must have a denominator somewhat less than $2\cdot 8199$, and there must be a D_{12} showing the own multiple displacement. This gives the second set in the list with a satellite separation $501\cdot 12$ due to $8\frac{3}{4}\delta$. The series formula is then calculated from $m=1, 2$. For the discussion of the succeeding lines see the lists and notes below. There is also a related $D(3.m)$ series as well as a considerable number of $d1-dm$ and $d2-dm$ combinations.

The probability of transitions from upper d levels (d_1) to upper p is seen to be abnormally low. In $D(2.m)$, D_{12} lines are seen from $m=1$ to 5, but $D_{11}(3, 4, 5)$ are not observed. They are present in the parallel $D(3.m)$ for $m=4, 5$, where $m=3$ lies in the ultra-red region. In this

series also we find representatives of D_{12} for $m=7, 8$. It is noticeable that the order $m=6$ appears to be totally disrupted in both $D(2.6)$, $D(3.6)$ as well as in $S6$.

The F^2 Series.

6. The constitution of the f term is not so definitely known as that of the d . The evidence, so far as it goes, tends to show that it is closely analogous to d , and that its extreme satellite term of lowest order is close to a multiple of Δ , and that this multiple is higher than that for the d . We shall employ this to get at least approximation to the position of the lower F lines. The series depending on d_1 for its limits will lie in the ultra-violet, but we should also expect to find a corresponding series with the same fm and limits depending on d_2 . We will make a first attempt with denominator $2+9\Delta$.

Here $2+9\Delta=2.907032$. The respective limits are

$$d_1 1, d_2 1 \quad 132460.12 + 2028.12$$

$$d_1 2, d_2 2 \quad 55330.09 + 502.02$$

The $F_1(1.m)$ and $F_1(2.m)$ are thus separated by 77130.03. The above considerations show that we should expect $F_{12}(1.2)$ somewhat less than 80520, and another 2028 ahead. We find such, as well as $F3$, at

$$F2 \quad 1n, \quad 80153.9 \quad \mathbf{2028.9} \quad 1, \quad 82182.3 \quad d\lambda = .01 \text{ on two lines}$$

$$F3 \quad 1, \quad 103488 \quad \mathbf{2032} \quad 1, \quad 1055.0 \quad d\lambda = .04 \quad ,, \quad ,,$$

with denominators 2.896105, 3.892030.

Both separations are within O.E. of these high wave numbers, and the intensities really indicate strong lines. In general, F lines have much closer satellites than the D . In this sub-group ZnF shows none, CdF indicates a very close one by its diminished doublet separation, EuF gives a quite definite one, due to 11 lines. We should then expect, also, satellites in Hg , i.e. F_{11} larger than F_{12} , and should not be surprised, in accordance with the abnormal complexity we have found in this element, to find several.

For $F(1.3)$ there is a possible F_{11} with a satellite separation of 107. Displacements of $20\delta_1$, $19\delta_1$, would produce separations of 107.62, 102.26 respectively.

The $F(2.m)$ being 77130.03 below $F(1.m)$ places the $F(2.3)$ about $26368 \pm$. This clearly settles the F_{12} , F_{11} at the observed

$$1, \quad 26375.42 \quad \mathbf{102.26} \quad 1, \quad 26177.68,$$

giving the exact $19\delta_1$ separation. These are good measures and enable us to reconstitute to the same exactness the F(1.3) lines. Also the F(1. *m*) lines give a $f_2 2 - f_2 3$ combination about $23344 \pm$ which we find at 23348.221. This, then, further provides a similar correction for F(1.2). The directly observed separation for F(1.3) is, however, 107—the $20\delta_1$ —although it may be 102 within O.E. There are, then, two possible cases, viz., $20\delta_1$ or $19\delta_1$ in F(1.3) with $19\delta_1$ only in F(2.3), for the persistence of satellite separations in parallel series, although usual, is not without exception. The values thus corrected are, then,

	(107).		$d\lambda$.	102.		$d\lambda$.
F ₁₂ 2	80151.87		−.03	...157.23		.06
F ₂₂ 2	82180.0	2028.12	−.04	...185.35		.04
F ₁₂ 3	103500.09		.02	...505.45		.07
F ₁₁ 3	607.71	107.62	.02	...607.71	102.26	.02
F ₂₂ 3	105528.21	2028.12	−.02	...533.57		.03

The 102 arrangement is sustained by a $3h\nu$ effect,

$$3 \times 26719.0 = 80157$$

It remains to determine the satellites or the F₁₁ for F₁₂(1.2), which are important as giving separations for the G series. Three possible lines, marked *a*, *b*, *c* in Table VII., for F(1.2) are present, with observed separations from F₁₂ of 122.2, 186.7, 296.6. The own multiples give the following:—

$$9\delta_1 \parallel 117.68; \quad 10\delta_1 = 130.75; \quad 14\delta_1 = 182.80; \quad 23\delta_1 = 299.84$$

As the observed λ are given to .1 or $dn=6.5$, the test holds for all within O.E., and none are excluded on this basis. It may be noted that if we take the separations on the corrected F₁₂ above, those on the 102 basis agree closely with $9\delta_1$, $14\delta_1$. Again, this basis is sustained for $\sigma=182$ by a $2h\nu$ effect, and for 299 by $4h\nu$ (Table VII., *b*, *c*).

$$2 \times 40171.44 = 80342.88 \quad d\lambda = .09$$

$$4 \times 20114.50 = 80458.0 \quad d\lambda = -.06$$

For further details as to the series and *ff* combinations, see the F list and notes below.

It may be noted that as 117.68 is 182.16 behind 299.84, the four lines in F₁(1.2) may be regarded as two inde-

pendent sets of one satellite, each with the same own displacement. Thus

F_{12}	80157.23	aF_{12}	274.91	
bF_{11}	340.03	182.80	cF_{11}	457.07 182.16

of which one may belong to the α system and the other to an independent one.

The G Series.

7. With f_12, f_13 as the limits of the G series, $G(2.m)$ will be in the visible spectrum and $G(3.m)$ for orders ≥ 6 . Any determination of the $G(2.m)$ is rendered difficult by the complexity of the f_2 satellites and the actual presence in the spectrum of numerous separations of these f_2 values, and of d_1d_2 sets. The allocation given in the list must be roughly correct, but the whole region shows such evidence of linkings with d, f separations and displacements that the exact details may have to be modified with further knowledge. The discussion will be taken on the list as it stands, and afterwards some examples of complexities will be taken in illustration. This is important as evidence of complexities actually existing in the spectrum. It will then be best to begin with $G(3.m)$ and look for $f_{13}-g_2, f_23-g_2$, *i. e.*, separations about 102.26. In the region for $m=6, 7, 8$ we find the sets reproduced as raw material after Table VIII. Here the figures in brackets denote the denominators as given by Rydberg's tables. An inspection shows at once that a regular series is indicated by those marked A and by those alone. The good measures for $m=7, 8$ are taken for the formula.

Satelloids.

8. The occurrence of wave-number differences amongst S2 and other lines between the measures of apparently the same line by two observers, greater than their O.E., has been already noted. Their appearance suggests the existence of an effect similar to that exhibited in copper, which for convenience I called the satelloidal effect. In copper * we find a very considerable number of examples of strong lines accompanied by numerous close companions,

* Phil. Mag. 2, 196, 26.

neither true satellites nor analogues of the very close sets in complex lines. These are such that their separations from the main line are always multiples of a constant $\cdot 57$ (or $\cdot 54$). If a similar effect is found to exist in mercury we must conclude that we are in the presence of a general constructional law of spectra. Its discussion is therefore of more importance than for the analysis of the mercury spectrum alone. Examples of the effect so noted—without any special examination of the whole spectrum—are given in the following table. The first thirteen deal with measures by different observers, differences, therefore, ostensibly due to different excitations. They are chiefly between Cardaun and Stiles, both very reliable, and showing differences depending on $2\cdot 7$.

C., D., P., S., Ly. denote, respectively, Cardaun, Déjardin, Paschen, Stiles, Lyman.

1. S. 27711·377 P. 16·61 S. 25·185	} $5 \times 2\cdot 761$	12. C. 44226·04 D. 27·60 P. 28·973	} $2\cdot 93$	21. S. 29827·86 S. 32·422	$10 \times \cdot 456$
2. C. 30626·20 S. 28·900		13. C. 44373·05 ⁽¹⁾ D. 75·02 P. 75·813 ⁽²⁾		22. P. 33268·64 P. 74·07	
3. S. 30971·558 C. 73·96		14. P. 22034·79 P. 37·61		23. P. 25356·87 ⁽⁴⁾ P. 59·14	$5 \times \cdot 454$
4. C. 31648·46 S. 51·316	$2\cdot 70$ $2\cdot 40$	15. P. 30133·45 P. 36·36	$2\cdot 82$ $2\cdot 91$	24. S. 24742·604 P. 43·04	$\cdot 45$
5. C. 33919·24 S. 22·003	$2\cdot 76$	16. C. 31920·28 C. 25·731	$2 \times 2\cdot 725$	25. C. 37651·18 S. 51·637	$\cdot 46$
6. C. 35104·16 S. 06·162	$2\cdot 00$	17. C. 33687·579 C. 88·351 C. 91·111	$2\cdot 76$	26. S. 38803·383 C. 03·895	$\cdot 51$
7. S. 35616·731 P. 22·11	$2 \times 2\cdot 69$	18. C. 35229·84 C. 40·65	$4 \times 2\cdot 702$	27. S. 41410·261 C. 12·12	$4 \times \cdot 465$
8. C. 36989·49 S. 92·230	$2\cdot 74$	19. C. 40023·65 C. 39·51	$5 \times 2\cdot 732$	28. C. 41523·71 S. 26·827	$7 \times \cdot 445$
9. D. 38741·49 P. 47·05	$2 \times 2\cdot 78$	20. C. 25092·883 ⁽³⁾ C. 93·349 C. 93·834 C. 94·307	$\cdot 466$ $\cdot 485$ $\cdot 473$	29. C. 44933·44 D. 34·45 P. 35·66	$5 \times \cdot 444$
10. C. 40112·12 S. 14·894	$2\cdot 77$			30. D. 53490·81 Ly. 94·8 ⁽¹⁾ P. 97·62 ⁽²⁾	$15 \times \cdot 454$
11. D. 44155·33 C. 60·60 P. 62·94 D. 63·52	} $3 \times 2\cdot 73$				

(1) (2) These sets are separated respectively by α , viz. :—9121·8, 9121·80.

(3) P gives a single line equal the mean.

(4) S gives ... 56·863; ... 59·138. sep. $2\cdot 275 = 5 \times \cdot 455$.

It might be objected that these were due to some systematic differences, but in general these observers agree very closely, and in the above those of Stiles are sometimes in defect and sometimes in excess of those of others. Examples 14 . . . 19 deal with pairs by the same observer. Here the duplicity is evident, and the observed separations will be more exact, as free from those errors. These first two groups refer to a separation about 2.74. The satelloidal effect, however, may be due to a still smaller constant of which 2.7 is a multiple, and this is indicated by Ex. 20, containing four close, equally-spaced lines by Cardaun at a mean separation of .47, whilst $2.7 = 6 \times .45$. Runge and Paschen give here three close companions separated by .473, .432 or mean = .453. The last eleven examples depend on this smaller value. Multiples of this are also indicated in companions in Ex. 1, 11, 12, 13, 17. The existence of the effect must therefore be regarded as established by the large number of consonant examples found. This being accepted, Ex. 3, 6 should not be included, as differing from the 2.7 by more than the O.E. The most reliable values should be those deduced from Cardaun's readings, viz., 2.725(2), .76(1), .702(4), .732(5), the figures in brackets denoting weights. The weighted mean is 2.726. Ex. 11 by D. gives 2.730(3); 14, 15 by P. give 2.82(1), 2.91(1). For the smaller values we similarly find .475(3), .456(10), .452(12), .454(5), .45, .46, .51, .465(4), .445(7), .444(5); 454(15) weighted mean $y = .4547$ whilst $6 \times .4547 = 2.726$. The agreement of the two sets is remarkable. Other examples will be found in the examples of linkages given below. The relation between the lines 1 and 2 in the list in § 1 is clearly of a satelloidal nature. The calculated separation for 698 is 9051.41, which is 5.03 behind the strong line of 2. This is due to $11y = 5.00$.

From analogy with the effect as found in copper we should then expect :

(1) That a line which is affected thereby must be one which contains p^2 as one of its terms, although in the present state of our knowledge, the presence of higher orders of p should not be excluded absolutely.

(2) That true link-values frequently occur between one line and a satelloid of another, which satelloid, however, is not necessarily itself observed. With good measures, if an approximate link differs little from a true one by a multiple of $y=4547$ it should be taken, provisionally at least, as a true link thus modified. There are large numbers of these cases, some of which are noted in the next section, and also in the notes to the tables.

Links.

9. In examining the whole spectrum for separations differing by a few units from α, β, γ an exceedingly large number of such cases was found. Evidence was obtained that they occur also as links. This is completely in accordance with the fact that the ν separations of p terms also serve as b links. The complete analysis of the whole spectrum would require the discussion of the linkage systems for all the recognized link values. This would be a big undertaking with such a rich spectrum as that of mercury, with its possibly complex sets of links, and is not necessary for the isolation of the normal neutral or ionized series, but some attention should be paid to the b links, if only to distinguish them from the equal doublet ν separations.

An important new fact emerges, viz., that ionized links are attachable to neutral lines, as well as neutral links to ionized lines. Some illustrations of the first statement are given below, whilst support for the second is given by the very complete set $e.S^2m$, where e is the neutral $e=20612.06$. In the simple excitation of a neutral line an electron is raised to a higher level (say) $i pm$. In a more complicated excitation a second electron (that which would act for an ionized line if the first were expelled) may be raised to its corresponding $ii p_1 2$, and then both fall to their corresponding $i s$ and $ii p_2 2$ levels. It is possible that the value of the $ii p_2$ level may be slightly affected by the presence of the far out $i pm$, thus modifying slightly the observed link value. If this is so we may have at our disposal a means of studying directly the interatomic actions of electrons.

All links yet recognized are calculable from series constants (the lowest p, s, d terms and the ν separation). Their appearance in any case, the $b=\nu$ link excepted, there-

fore definitely denotes a linkage. The separations now to be considered are all, on our initial supposition, either α separations or b links. There is nothing, then, to distinguish an individual case as between the doublet separation of two bi-term lines or a link. But one distinguishing feature of linkages is that sets of successive links occur, a phenomenon which cannot happen with a normal series separation. Moreover, when the individual links appear slightly modified, the modifications in a complete chain often annul one another, and the sum of the observed is equal to the sum of the corresponding normal links. In any case a long set of such close link values amongst lines which are not crowded together will indicate their link nature. The number of such sets in this spectrum is surprisingly great. I give here a few illustrations taken almost at random, but sufficient to show that these α , β , γ separations can appear as links. The numbers in brackets after a wave number give the separations from the next lines in the spectrum before and after, and serve as indicators of the degree of crowding in the region of the line.

A.

1, 26621.89 (3, 20) 0120.1 21.85742 (36, 76) 9120.1 1 iii 44862.07 (34, 72).

The third line is (748) S_2 2, with a separation .70 ($d\lambda = .03$) too small. The middle one has only been observed by B¹., but it serves to indicate the double linkage. If the third is the corrected (748) S_2 2, the link sum is $2 \times 9120.45 = 2\alpha - 270$, with the large satelloid value 2.72.

B.

1 iii	21511.164 (7, 40)	
3 i	30628.900 (130, 60)	9117.74
4 i	39752.755 (34, 11)	23.855
0 ii	48873.48 (109, 24)	20.73
1	57998.9 \pm 1.7 (86, 100)	25.4

C.

S_1 2	35104.16	
S_2 2	44933.44	9828.29
4	54760.4 (194, 72)	27.0
3	64591.1 (67, 113)	30.7
2	74421.4 (39, 78)	30.3

B. The last line is by Ly., and the ± 1.7 refers to equally probable values. As they stand, the sum of the separations is 4×9121.93 . Correcting the last line to ... 8.48 ($d\lambda = .01$ on 1724.2) makes the sum exactly 4α . No β or γ links are found to these lines.

C. This is a chain continuing the S_1 2 and γS_2 2, with the same separation. As in Ex. B, in the complete chain the

modifications are annulled, and the total separation is 4×9829.31 . With the high W. N. the O.E. are considerable, and the 9829.3 is not necessarily exact. But the individual lines are well isolated from others, and the agreement is sufficiently close to establish the fact that 9829 behaves also as a link. The first is a genuine ν or exact $\gamma - y + .06$; the last three are b links. The multiple 4γ requires the last line to be 1.44 greater, or $d\lambda = -.02$ on $\lambda = 1343.7$.

D (four sets).

(The 98 in the 9829 and the intensities are omitted.)

10004		10591		10802		14193	
19826.7	22.7	i 20420.4	29.4	i 30635.96	33.9	ii 24022.18	29.1
29654.5	27.8	30247.32	26.9	ii 30466.0	30	33851.7	29.6
39487.44	32.9	i 40082.21	34.39	40291.24	25.2		
i 49318.76	31.32						
24.60							
Mean...	9828.69	... 30.15	9830.40	9829.70		9829.35	

The sets all start from ultra-red lines, the first three by McL. and the last by W. The lowest line in the first, by P. and D., show the sateloid effect 5.84 , $13y = 5.91$. A sateloid $-4y$ on D's would give a mean value 9829.70 or $\gamma - .03$. In the second the deviations in the mean from the normal cannot be met by O.E. on the first line. But the whole, with Ex. C., are sufficient to show that 9829 behaves as a link as well as a doublet separation.

E (two sets).

3	10802 (38, 47)		1	13216.2 (72, 24)	
1	20134.2 (19, 14)	9332.2	1	22548.34 (8, 11)	9332.1
4 ii	29469.25 (34, 12)	35.0	2n	31880.68 (89, 9)	32.34
3A	38803.895 } (23, 22) Cd.	34.64	2 ii	41212.2 (57, 21)	31.84
	383 } S.	34.13	0 i	51040.98 (26, 53)	9828.46
					9333.63, ... 46

These involve the β separation. The first set starts from the same line as in Ex. D, 3, the last being the arc line S_2^{34} , the two measures by Cd., S. respectively. The S. measure gives the exact mean β , but the Cd. as S_2^3 gives the exact ν_1, ν_2 in S^{34} .

F.

2	26588.854 (15, 20)	9117.15	} 2, 35106.005 {	9122.26	5 i 44828.27 ($73\frac{3}{4}$) S ₂ ² 2
8 i	26375.26 (16, 17)	9330.74		9331.88	0 i 45037.88 (17, 38)
1	25876.847 (38, 21)	9829.16		9827.85	1 i 45533.86 (30, 17)

Several interesting points arise with these lines.

(a) The series inequality $9829.16 + 9122.26 = \alpha + \gamma + .08$.

(b) 44828 is ($73\frac{3}{4}\delta$)S₂2 and 26375 is F₁₂²(2.3), and the two cannot come in the same chain. S. gives two close lines 26376.818 and .79.027 separated by 2.209.

(c) Also another pair by S. 25876.847, . . . 73.094, separated by $3.75 = 8y + .11$.

(d) The presence of the p_2 being assured by S₂, these separations can be written.

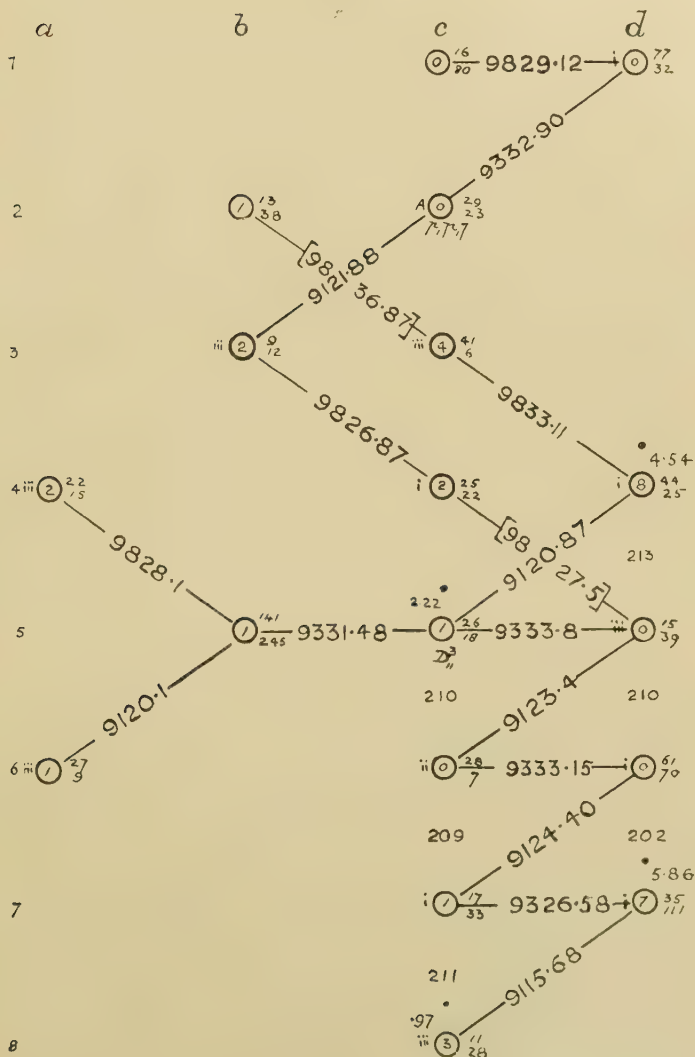
$$\begin{array}{ll}
 \alpha - 10y - .10 & \alpha + y \\
 \beta - 6y + 0 \text{ (2.72)} & \beta - 1.53 ? \\
 \gamma - y - .06 & \gamma - 4y + 0
 \end{array}$$

G.

This is a linkage map on a more considerable scale. It doubtless contains some false—*i. e.*, chance—links, but it affords very definite evidence for ionized links attached to neutral lines. It also illustrates an arrangement of frequent occurrence whose interpretation may be of importance.

We get direct evidence of the satelloidal effect in the lines at c_5 , c_8 , d_4 , d_7 from the recent measures of Paschen. At d_4 P.'s measure 48695.216 is separated from D.'s by 4.54, or an exact $10y$. We note, also, that the links to these are $9120.87 = \alpha - 2y - .02$ and $9827.57 = \gamma - 2y - .26$. We must accept the first, but the second is more doubtful with a succeeding $9836.84 = \gamma + 16y - .08$. At c_5 P. gives a line 2.22 behind it with $5y = 2.27$. At d_7 , c_8 , P.'s values are $5.86 = 13y - .05$ and $.97 = 2y + .06$ behind those of D. Here, also, the attached links are

MAP.



a. 21419.2; 21127.8.—b. 29529.81; 29258.261; 30247.41.—
c. 37884.02; 38380.24; 38866.65; 39085.15; 39578.89; 39789.34;
39998.09; 40208.92.—d. 47713.14; 48699.76; 48912.7; 49122.49;
49324.60.

$9326.58 = \beta - 6.84$ with $15y = 6.82$ and $9115.68 = \alpha - 6.15$ with $13y = 5.91$, of which the first at least may be accepted as possible.

The line at $c5$ is quite definitely D_{11}^{313} . As we have seen, it is also linked by α to a $2y$ -satelloid of D 's 48699.76 at $d4$. The 9333.8 is β within the O.E. of the line 48912.7 ($d5$). In other words, we find two ionized links to the neutral D_{11}^3 . The 9331.48 back is $\beta - 4y - 12$. The $b5$ is an arc line only observed by K. R. and E. V. with the considerable possible error of 1.8 . It has been allocated by P. to a combination $p_2^{31} - p_2^{32}$, in which, I think, his P_2^{32} may be doubtful. If his allocation is correct, 9331 must be a chance coincidence; if the link is real, $\beta - 4y$, $b7$ is $\beta.D_{11}^3(13)$, and not the pp combination. The back lines from it are γ , α within the O.E. of the lines at $a4$, $a6$.

The line 38380.24 at $c2$ is $p_1^{31} - p_1^{37}$ with the exact α back to $b3$. Also the two links to $d1$, 9332.90 and 9829.12 , are $\beta - 52$, $\gamma - 55$, thus forming a parallel inequality, and definitely giving $c1$ as γ . ($p_1 p_1 7$ or $c3$). β . The set, however, cannot be linked to D_{11}^{13} , and one at least of the defective 9826.87 , 9827.5 to $C5$, $d5$ will be false. This is indicated in the map by [], 9826.87 is $\beta - 2.80$, with the big satelloid 2.72 .

Lastly, we note the curious appearance of alternate $-\alpha$, $+\beta$ links successively from $d4$ downwards. If $d4$ be written X , the linking means that the other lines depend on $\alpha.X$, $\alpha.X.\beta$, $2\alpha.X.\beta$, $2\alpha.X.2\beta$, $\dots 4\alpha.X.3\beta$. But the arrangement may be interpreted in another way, as sets of lines differing by an amount close to 213 . To illustrate, suppose for the moment $c5$, $d4$ were $p_1^2 - t$, $p_2^2 - t$. The lines in the map would be constituted by successive displacements in the t term of the same amount. Here such displacements would be positive, and the succeeding shifts would show decreasing amounts, as, indeed, the figures in the map indicate. This appearance of large numbers of separations in special regions near those of d or f satellites is quite common in general, and indicates that normal D or F lines are in the neighbourhood. In the present case this explanation is not tenable, for $c5$ is certainly an arc line, and almost certainly is D_{11}^{313} . To produce a shift of 210 in the $d_1(13)$ would require a displacement of the denominator from 13.9 to 17.8 , and is quite out of the question.

H.

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
1.		1 iii 22649·73	9830·6	2 iii 32480·3 9121·7 0 A 41602·0
	9121·7		9334·24	
2.	0, 13528		5 A 31983·97	D_{22}^{32}
	9333·5		9122·41	
3.		2 i 22861·56		
	9833·0			
4.	2, 13028·5			

Here again at *b1* we find a satelloidal indication. S. gives three lines, all of class E3, and E.V. two.

1 iii 22644·255			1, 22639·1
1 iii 49·733	5·478	12 <i>y</i> = 5·456	1, 42·2 3·1
1 iii 60·268	10·535	23 <i>y</i> =10·46	

All the links are normal except those on *c2*, which is D_{22}^{32} . These may be written $\beta + 2y - 0.9$ and $\alpha + y + 1.3$, but if the satelloidal effect is really present it must be due to the *p2* present in the links themselves. 13528 has been allocated by Paschen to $G_1^2(4.9)$. We get a parallel inequality from *b1* to *c1*, *c2*, viz. :—

$$9830.6 - 9334.24 = \gamma - \beta + 1.10.$$

Thus, putting $D_{22}^{32} = D$,

$$c1 = \beta \cdot D \cdot \gamma + 1.10, \quad d1 = \beta \cdot D \cdot \alpha \cdot \gamma + 0.$$

This whole set is a very clear example of linkage to a neutral line by ionized links.

I.

1	9121·0	2	9334·62	D_{23}^{35}	9830·57	10	9120·64	8	9330·1	0
				D_{22}^{35}	9119·62	0	9830·84	10		

The numbers in the line places are intensities.

$$D_{22}^{35} = 41658.49, \quad D_{22}^{35} = 41664.74.$$

The lines in the fifth column are 60609·7 by C. and 60615·6 by Ly., and are both of similar intensity. At first sight they might be taken as measures of the same line, but they differ by more than their average amount. The arrangement shows that one is linked to the main D_{22}^{35} and the

other to the satellite $D_{23}5$, in each case by series inequalities, viz. :—

$$9830\cdot57 + 9120\cdot64 = \gamma + \alpha - \cdot26 \quad d\lambda = 0$$

$$9119\cdot62 + 9830\cdot84 = \gamma + \alpha - 1 \quad d\lambda = \cdot02$$

Also $9121\cdot0 + 9334\cdot62 = \alpha + \beta + \cdot4 \quad d\lambda = \cdot06$

or the first chain as a whole $= 2\alpha + \beta + \gamma + \cdot1$ with all modifications annulled. $d5 = 3776$, so that the link modifications can be accounted for by displacements in the $d5$ terms. Thus $9119\cdot62$ is $\alpha - 2\cdot21$, and $6\delta_1$ shifts $2\cdot26$; $9120\cdot64 = \alpha - 1\cdot20$, and $3\delta_1$ shifts $1\cdot13$. The agreement is thus very close within O.E., but, unfortunately, the evidence cannot be considered decisive, since the own shifts on $d5$ are so small and the O.E. on the higher wave numbers are so large. Moreover, all our preconceptions, although dangerous guides, go against such strong lines being really linked to lines of order $m=5$. The importance of this discussion lies in the fact that 60609, 51489 (the fourth and fifth in the first row) have been allocated by Carroll to $-S^2_1$, an allocation accepted by Paschen.

J.

	<i>a.</i>		<i>b</i> _{McL}		<i>c.</i>		<i>d.</i>
1.	1	9121·4	} 10 S ₁ ³³	9832·52	4 ii	} 1 i	9120·96
2.							
3.	4	9330·9		9124·71	5		9828·77
4.			} 5	9828·3	} 1	} 1 n	
5.				9121·3			
6.				9333·6			

Col. *a.* (9186·1; 8976·6) McL.—*b.* 18307·456; 17603·9.—*c.* 28139·978; 27432·173; 26725·195; 26938·5.—*d.* 37260·94. The numbers in line positions are intensities.

This is given to illustrate a similar arrangement with a S3 line. It can be seen that where the links are not normal they can be made so by satelloidal considerations. Stark gives a line 7·4 less than $c3$. This is possibly due to an own displacement in $s2$, since $s2 = 7\cdot04$.

I add a few further indications excerpted from larger maps, illustrating ionized links to neutral series lines.

$$(1) \quad 9333\cdot34 \quad D_{11}{}^{34} \quad 9121\cdot59 \quad (3 \text{ iii}) \quad (1) \left\{ \begin{array}{l} 9121\cdot27 \quad S_2{}^{33} \\ 9829\cdot75 \quad (1) \end{array} \right.$$

$$D_{23}{}^{33} \quad 9121\cdot89 \quad (1 \text{ ii})$$

$$(2 \text{ i}) \quad 9829\cdot7 \quad S_3{}^{34}$$

$$D4=35659\cdot49; D3=37672\cdot32; S3=34548\cdot85; S4=40571\cdot17.$$

The foregoing examples afford indisputable evidence that the α , β , γ separations appear as links, and, moreover, as links attachable to neutral lines as well as to ionized. The examples given are a sample only of the very large mass of data at disposal. The attachment to neutral lines shows also that they cannot enter there as displacements in a bi-term line, and thus directly supports the supposition of § 1 that their origin is due to independent p_2^+ terms.

TABLE I.

The p_2 separations from p_1 (2, 3, 4).

$$p_1 2 = 92024.56; \quad p_1 2 - = 30.557.$$

δ .	$p2$.	$p3$.	$p4$.
67	2721.08	1183.12
68	63.67	1201.44
69	9051.41	2806.29	19.75
$69\frac{1}{4}$	86.59	16.95	24.33
$69\frac{1}{2}$	9121.80 α	27.62	28.91
$69\frac{3}{4}$	57.03	38.28	33.50
70	92.26	48.94	38.08
$70\frac{1}{4}$	9227.51	59.63	42.67
$70\frac{1}{2}$	62.80	70.32	47.25
$70\frac{3}{4}$	98.09	81.01	51.84
71	9333.41 β	91.70	56.42
$71\frac{1}{4}$	68.73	2902.38	61.02
$71\frac{1}{2}$	9404.08	13.08	65.62
$71\frac{3}{4}$	39.45	23.79	70.23
72	74.84	34.51	74.81
$72\frac{1}{4}$	9510.30	45.21	79.42
$72\frac{1}{2}$	45.65	55.92	84.02
$72\frac{3}{4}$	81.11	66.66	88.61
73	9616.58	77.40	93.21
$73\frac{1}{4}$	52.06	88.12	98.81
$73\frac{1}{2}$	87.56	98.84	1302.42
$73\frac{3}{4}$	9723.08	3009.57	07.02
74	58.61	20.31	11.63
$74\frac{1}{4}$	94.17	31.04	16.24
$74\frac{1}{2}$	9829.74 γ	41.77	20.85
$74\frac{3}{4}$	65.31	52.50	25.47
75	9900.90	63.24	30.09

TABLE II.

 $S^2(2.m).$

$$92024.56 - 4R/\{m + .835829 - .119166/m\}^2.$$

$$p_1 2 - = 30.557; p_2 2 - = 35.18(68\delta) \text{ to } 35.56(74\delta).$$

$sm - m.$	I.	$n.$	$v.$	$d\lambda.$
63.26				
1.*		[-57495.30] ⁽¹⁾		
	1 i	-48371.96	9123.34	.06 α
*	0 ii	-47772.65	722.65	-.02 73 $\frac{3}{4}$
14.865				
2.*	10 i	35104.16		
	0 iii	44155.33	9051.17	.01 69
*	7 i	190.755	086.59	0 69 $\frac{1}{4}$
	7 i	226.04	121.88	0 α
?	7 i	373.05	268.89	? α
	7 ii	542.88	438.72	.03 71 $\frac{3}{4}$
??	0 i	611.24	507.08	.16 72 $\frac{1}{4}$
	0 i	684.8	580.6	.03 72 $\frac{3}{4}$
	5 i	828.27	724.11	-.05 73 $\frac{3}{4}$
	1 ii	862.07	757.91	.03 74
	10 i	933.44	829.28	γ γ
?	0 i	45000.6	896.4	-.2 75
5.8147				
3.*	1	61578.06		
	4	70671.4	9091.3 ⁽²⁾	-.09 69 $\frac{1}{4}$
	1	700.05	121.99	.00 α
	2	71407.86	829.80	.00 γ
2.865				
4.*	3n	[73030.73]		
?	3n	82447.0	9416.3	-.18 71 $\frac{1}{2}$
	3	877.5	846.8	-.2 γ
1.616				
5.		[79036.66]		
*	1n	88090.2	9053.5	-.02 69
	1n	160.1	123.4	-.02 α
	1	292.4	255.7	.09 70 $\frac{1}{2}$
*	0	550.4	513.7	-.03 72 $\frac{1}{4}$
	1	621.1	584.4	-.02 72 $\frac{3}{4}$
	0	754.8	718.1	.06 73 $\frac{3}{4}$
*	2	865.2	828.6	.01 γ

$sm - m.$	I.	$n.$	$v.$	$d\gamma.$
1.0045				
6.	*	[82580.94]		
	1	91734.7	9153.8	.04 69 $\frac{3}{4}$
	0	954.0	373.1	-.05 71 $\frac{1}{4}$
.665				
7.		[84848.02]		
	0	93967.3	9119.3	.03 α
	1	94437.6	589.6	-.08 72 $\frac{3}{4}$
	1	509.0	661.0	.08 73 $\frac{1}{4}$
	0	562.6	714.6	.09 73 $\frac{3}{4}$
.453				
8.	*	[86385.98]		
	1	95483.6	9097.7	-.1 69 $\frac{1}{4}$
	2	96182.05	796.07	-.01 74 $\frac{1}{4}$
*	1	237.1	851.2 ⁽³⁾	-.2 γ
.336				
9.	*	[87477.28]		
*	2	96646.4	9169.1	-.13 69 $\frac{3}{4}$
	1n	777.3	300.0	-.02 70 $\frac{3}{4}$
	1	918.0	440.7	-.01 71 $\frac{3}{4}$
10.		[88279.67]		
	2	97503.9	9224.2	.03 70 $\frac{1}{4}$
11.		[88882.86]		
	3n ?	98020.0 ⁽⁴⁾	9135.1	-.13 α
	1	212.5	327.6	.06 β
	0 ?	483.4	598.5	-.17 72 $\frac{3}{4}$
	1 ?	6 ⁽⁵⁾	734.4	-.12 73 $\frac{3}{4}$

(1) Disrupted to $(\pm \delta_1) S_1(\pm \delta_1)$.(2) Estimated from C.'s $S_1 = 61580.1$, the same observer. Paschen's intensities are 5, abs. 9, 2.(3) Or $74\frac{3}{4} \delta_1 d\lambda = .15$.(4) Is probably $P^3(1.7)$.(5) Is $P^3(1.9)$.* See $n\hbar\nu$ list.

2. 2847·83 Cd.; 2264·03 D.; (...62·215; ...60·41; ...52·92) Cd.; ...44·40 E. H.; (...40·89; ...37·2; ...30·4; ...28·36) D.; ...24·82 Cd.; ...21·5 D.—
 3. 1623·955 P.; 1415·0; (...14·427; 00·406) P.—4. 1212·9; ...06·6.—
 5. 1135·2; ...34·3; ...32·6; ...29·3; ...28·4; ...26·7; ...25·3.—6. 1090·1;
 ...87·5.—7. 1064·2; ...58·9; ...57·5.—8. 1047·3; ...39·695 P.; 39·1.—
 9. 1037·4; ...33·3; ...31·8.—10. 1025·6.—11. 1020·2; ...18·2; ...15·4;
 ...14·0

Combinations.

s1—s2	4, 1080·1	92584
s2—s3	1, 3776·259	26472·742

Notes.

The oun shifts are given in the table. The limit p_1 is determined as explained in the text. The formula is determined from this and $m=2, 3$.

$n=1$. The extrapolated value of the denominator for $m=1$ is 1·716663, and we should expect a value slightly less, or $s1-p2$ about 57400 \pm . We find here the sets:—

Ly.	6 57466·4	63·1	8 57529·5
C.	1 58·1		4 27·5
	9829·4; ...21·1		9339·7; ...37·9
D.	0 47636·98 iii?		On 48189·64 ii?

The mean of Ly and C. for the first gives ... 62·2, with doublet separation 9825·2. They suggest at first sight ($\pm\delta_1$) S_1 ; but since here the W.N. is $s1-p2$ (not $p2-s1$) this would require the $(+\delta_1)\beta$ separation on the right and $(-\delta_1)\gamma$ on the left, whilst the opposite is clearly indicated. The difficulty is explained by the fact that $s1-$ is 63·26. The conditions are then met by the double displacement $(\pm\delta_1)/(\pm\delta_1)$ shifting $63·26-30·56=32·70$, or 65·40 for the two. We then get not only the observed separation of the two sets, but also the $9333·41+4·79=9338·20$ and $9829·74-5·02=9824·72$ in their proper positions. We can then calculate the true S_1 from the more accurately measured $(-\delta_1)S_2(-\delta_1)=-48189·64$. Thus

$$(-\delta_1)S_1(-\delta_1)=-48189·64-9338·20=-57527·84.$$

Also $p_1(-\delta_1)=92024·34+30·61=92054·95$;

whence $s/(-\delta_1)=149582·79=4R/\{1·712577\}^2$

$$s1=4R/\{1·712577+362\}^2=149519·64$$

$$S_11=-57495·30.$$

While this is not seen, two corresponding S_2 lines are, viz. :—those in the table. We have here a very striking example of a normal line wholly disrupted into a very common arrangement of equal—like or unlike—displacements on both terms. The above value of S_1 is subject to the same O.E. as that of 48189. The value of $(\delta_1)S_1(\delta_1)$ calculated from this S_1 is 57462.45, practically the mean of Ly. and C., whilst $(\delta_1)S_2(\delta_1)$ is $(\quad)S_1(\quad) - 9824.72 - 47637.73$. The measure by D. is .75 less, or $d\lambda = .04$ between his two lines.

Although S_1 is wholly disrupted, we find a line linked to it by the neutral $e = 20612.06$, viz., 1 i, 36883.271 separated from it by 20612.03, practically the exact e i. The corresponding $s1 - p_1 3 = P_1(1.3)$ is also found. We get, also, a very striking illustration of the general relation $E = nh\nu$ for $n = 3$ in the observed line

$$1 \text{ i } 19165.044 \quad \text{or} \quad \frac{1}{3} S_1 - .05.$$

Also for S_2

$$1, \quad 2 \times 24098.9 \text{ E.V.} \quad = 48197.8 \quad \mathbf{9297.5} \quad (70)\frac{1}{4}\delta \quad d\lambda = .01$$

$m = 2$. The following collaterals are found, comparing Stiles with Stiles (35106.16) :—

	Obs.	
$(-\delta_1)S_1(\delta_1) = 35751.58$	$\dots 54.233 - 6y + .07$	3 2848.774
$(\delta_1)S_1(-2\delta_1) = 35045.88$	$\dots 47.739 - 4y - .05$	2 i $\dots 52.415$
? $(-\delta)S_1(2\delta_1) = 35258.12$	$\dots 257.451 + y - .22$	1 $\dots 35.448$
Cd. $(-3\delta_1)S_1(3\delta_1) = 35240.44$	$\dots 240.65$	$\frac{1}{2} \dots 36.80$

Further, if the $2h\nu$ effect is admitted, the additional S_2 lines come in:—

1 4510.5 Stk.	$2 \times 22164.8 \pm 1 = 44329.6 \pm 2$	$\mathbf{9225.4}$.2	$70\frac{1}{4}$
2 iii 4506.704	$2 \times \dots 82.964 = \dots 365.928$	$\mathbf{9261.77}$.1	$70\frac{1}{2}$
1 iii 4499.8 E.V.	$2 \times \dots 217.5 \pm .5 = \dots 435.0 \pm 1$	$\mathbf{9330.84}$.25	71

$m = 3$. The far more accurate measures of P. have been inserted. Bl. gives two collaterals, 1,61512.0, 1,61648.5, shifted 68 on either side of S_1 , whilst $2\delta_1 / -\delta_1$ shifts $61.12 + .5.81 = 66.93$. They are then $(\pm 2\delta_1)S_1 3(\mp \delta_1)$.

Also, if $2h\nu$ be admitted,

$$2 \times 35669.186 \text{ Cd.} = 71338.37 \quad \mathbf{9760.31} \quad -.07 \quad 74$$

$m=4$. The calculated S_1 shows two very doubtful S_2 , and is itself disrupted ; the corresponding line in S(3.4) is visible. It is emitted as $h3\nu$, $2h\nu$ however, viz. 3×24343.34 ; 3×36525 .

$$1 \quad 1367.2 \quad 73142.2 = (-\delta)S_1(-\delta) \quad d\lambda = -.01$$

On the $2h\nu$ basis

2 ii	2433.87 D.	$2 \times 41074.37 = 82148.74$	9118.0	.1	α
1 iii	2424.46 D.	$2 \times 41233.78 = \dots 467.56$	9436.8	.08	$71\frac{3}{4}$
0	2421.35 D.	$2 \times \dots 286.73 = \dots 573.46$	9542.7	.09	$72\frac{1}{2}$
1 i	2417.16 D.	$2 \times \dots 358.29 = \dots 716.58$	9685.8	.05	$73\frac{1}{2}$

The first, 41074, is also $S_2(3.9)$.

$m=5$. The following collaterals are noted :—

$1n$,	1264.7	79070.1	$(-\delta_1)S_1(+\delta_1)$	$d\lambda = -.07$
$1n$,	63.7	79132.7	$(-3\delta_1)S_1(3\delta_1)$	$d\lambda = .00$
$1n$,	64.1	78982.0	$(2\delta_1)S_1(2\delta_1)$	$d\lambda = -.05$

The $s5$ — are now, and beyond $m=5$, comparable with O.F. Those given here may therefore err by one oun on sm . All the S_2 are successive lines in C.'s list.

$m=6$. This even order seems to show no collaterals except, possibly, $(\delta)S_1(-\delta) = 82454.84$. An observed 82447.0 may be a merge of this and S_24 .

$m=7$. Doubtful collateral

$$(-\delta)S_1(-\delta) = 84961.8 d\lambda = -.14.$$

$m=8$. The O—C values may be partly due to formula errors. If the true S_1 be that suggested by 2×43194.63 , the formula error is 3.32, $d\lambda = -.03$ and the separations are then more closely met.

On $2h\nu$ basis

$$0 \text{ ii} \quad D. \quad 2 \times 47755.07 = 95510.14 \quad \mathbf{9124.2} \quad -.05 \quad \alpha$$

$m=9$.

	Obs.	
$(\delta_1)S_1(\delta_1) = 87447.09$	$\dots 50.8$	$d\lambda = -.05$
$(2\delta)S_1(2\delta) = 87235.50$	$\dots 37.2$	$= -.02$

With these high orders the S and D lines come close together. There are several other near possible collaterals, but they may be related to D9.

TABLE III.

S(3.m).

S(4.m).

$$p_1 2 - p_1 3 = 49221.09; p_1 3 - = 9.6708.$$

$$p_1 3 - p_1 4 = 18052.33; p_1 4 - = 4.2625.$$

1, 2. See P(1.3), P(2.3).

2. See P(2.4).

5.8147

3. [12356.97]

- [5695]

1 15376.89 **3019.92** .11 74
2.865

4, 1 23808.5 - .09

[5755]

[7.98]

? 1 26573.232 **2765.25** -.2 681 613.0 **805.0** .18 692 ii 624.3 **816.4** .08 69½2 A 656.782 **838.80** -.07 69¾1 677.606 **869.62** .09 70½3 ii 806.584 **998.60** .03 73½* 1 829.4 **3021.4** -.1 74

1.616

5. [29816.27-.7]

5. [11763.3]

* 1 32772.23 **2955.96** -.02 72½3 13029 **1265.7** 0 71½* 3 ii 825.16 **3008.89** .06 73¾4 900.46 **084.19** .03 75½2 922.23 **105.96** .00 76

1.004

6. * [33360±]

6. [15307.2]

1 36123.0 **2763** 0 681 i 16500 **1192.8** -.2 67½2 ii 535 **227.8** -.4 α 1 i 573 **265.8** .07 71½2 ii 593 **285.8** .6 72½2 i 615 **307.8** .3 73¾

.665

7. [35627.06-.13]

7. [17574.60]

3 ii 38457.30 **2830.24** -.17 α 3 i 18803.47 **1228.87** .00 α 0 ii 500.20 **873.19** -.20 70½4 i 821.5 **246.9** -.09 70½0 ii 518.05 **891.00** .05 β 1 i 834.3 **259.7** -.4 71¼2 i 881.9 **307.7** .2 73¼? 1 i 903.3 **328.7** .7 75

453

8. [37164.89]

8. [19112.56]

0 ii 39908 **2743** -.05 67½2 20328.6 **1216.0** -.2 68¾0 ii 981.39 **816.50** .02 69¼1 415.2 **1302.6** .05 73½1 iii 40207.95 **3043.06** .09 γ 2 n i 420.4 **307.8** .2 73¾2 ii 237.24 **072.35** .09 75¼2 n 443.067 **330.50** .10 75

.336

TABLE III. (cont.).

S(3.m).				S(4.m).			
9.	[38256.19]			9.	[20203.86]		
1 ii	38258.91	2.72 =6 γ	0	2	21419.2	1215.3	-.02 68 $\frac{3}{4}$
2 ii	41074.37	2818.18	-.07 69 $\frac{1}{4}$	1	442.1	238.2	-.02 70
2 ii	212.52	956.33	-.02 72 $\frac{1}{2}$?2n i	445.714	241.85	.17 70 $\frac{1}{4}$
1 iii	233.78	977.59	.00 73	1	483.9	280.0	-.1 72 $\frac{1}{4}$
0	286.73	3030.54	.03 74 $\frac{1}{4}$	1 iii	21511.164	307.30	-.06 73 $\frac{3}{4}$
10.	[39058.58]			10.	[21006.25]		
1 ii	60.40	1.81 =4 γ	-.12	1 iii	226.4	220.2	-.1 69
1 ii	780.35	2721.79	-.06 67	1 iii	257.563	251.31	-.10 70 $\frac{3}{4}$
4 i	41825.44	766.86	-1.8 68	2 ii	266.818	260.57	-.10 71 $\frac{1}{4}$
0 i	847.33	788.75	-.21 68 $\frac{1}{2}$	1 iii	312.716	306.47	-.1 73 $\frac{3}{4}$
0 ii	861.5	803.0	.1 69				
0 i	871.69	813.11	.2 69 $\frac{1}{4}$				
1 ii	949.87	891.29	.02 β				
0 i	42039	980.4	.2 73				
11. 0 i	39663.21		.02	11. 2n i	21610.4		.1
1 i	42532.01	2868.80	.08 70 $\frac{1}{2}$	2 iii	22811.222	1200.8	.1 68
(4) i	620.85	957.64	-.09 72 $\frac{1}{2}$	2 i	861.561	251.1	.1 70 $\frac{3}{4}$
3 i	693.84	3030.63	.02 74 $\frac{1}{4}$	1	870.5	269.1	.2 71 $\frac{3}{4}$

S(3.m). 3. 6501.47 P.—4. 4199.1; 3762.122; ...56.6; ...55.0 Stk.; ...51.737; ...47.401; ...41.7; ...29.399; ...26.3.—5. 3150.58 K. R.; ...45.56 P.; ...38.69 K. R.; ...36.68 E. H.—6. 2767.6.—7. 2599.51; (...96.61; ...95.41.—8. 2505; ...00.41; 2493.23) D.; ...86.32 P.; ...84.51.—9. 2612.99; 2433.87; ...25.71; ...24.46; ...21.25.—10. 2559.37; 2392.74) D.; ...90.16 St.; (...88.91; ...88.1; ...87.52; ...83.07; ...78) D.—11. (2520.47; 2350.45; ...45.55; ...41.54) D.

S(4.m). 5. 7673 W.—6. (6059; ...46; ...32; ...25; ...17) Bl.—7. 5316.87 W.; ...11.7; ...08.0; 5294.7; ...88.7.—8. 4917.9; 4897.1 W.; ...95.8; ...95.45 W.—9. 4667.5; ...62.6 W.; ...61.635; ...53.6 W.; ...47.452.—10. 4499.8; ...98.0; ...91.603; ...89.732; ...80.496.—11. 4626.2; 4382.580; ...72.930; ...69.6.

Notes.

$m=3$. If the separation is the correct 3020.21, the correct S_1 should be .29 less and =12356.68. Instead of this are found two lines on either side displaced ($\pm\delta_1$)S ($\pm 2\delta_1$), shift = 9.67 + 11.63 = 21.30. Thus

	Obs.	
(δ_1) S_1 (-2 δ_1)=12335.38	...36	1, 8104
(- δ_1) S_1 (2 δ_1)= ...77.98	...77	2, 8077

In S(2.3) were found ($\pm 2\delta_1$) S_1 ($\mp \delta_1$).

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$m=4$. The value deduced from S(2.4) is 23809.64. This gives exact ν with the 26573. The observed is 23808.5. The value in [] used as S_1 is the value deduced from the accurate measure of the collateral $(2\delta_1)/(-6\delta_1)$ given below. All these are within O.E. of S(2.4). In the neighbourhood are found

	Calc.	Obs.	
$(2\delta_1)S_1(-6\delta_1)$	= 23771.45	...71.452	1 4205.546
$(\delta_1)S_1$	= 23798.31	...98.9	1 ...00.8
S_1	= [23807.98]	...08.5	
$(-2\delta_1)S_1(-2\delta_1)$	= 23821.59	...21.646	2 ii 4196.684
$(-3\delta_1)S_1(\delta)$	= 23848.45	...48.367	1 i ...91.982

23771, 23821 are mutually displaced by $(\delta)/(-\delta)$. In S(2.4) we found $(-\delta)/(-\delta)$. The agreement in these very accurate measures, with such large own shifts, is remarkably close. 26646 or $(69\frac{3}{4})S_2$ is given by Bl. as an arc line. But Steinhausen gives it as enhanced. Also E.V. and E.H. give it intensity 4 in the spark to Stiles's 2 in the arc.

$m=5$. The S_1 is taken .7 larger than that deduced from S(2.5). The following collaterals have been noted

		Obs.	
$(-\delta_1)S_1(\delta_1)$	= 29827.56	...27.36	$D_{11}(3.5)$ 1 3351.61
$(-2\delta_1)S_1(-2\delta_1)$	= 29832.38	...32.42	1 iii 3351.098

They are No. 22 in the satelloid list.

S(3. m).

S(4. m).

$m=6$.

This even order, as in S(3.6), gives no observed line, no evident collaterals, and few S_2 .

The S_2 are a set of five successive lines observed by Bl. alone.

$m=7$.

	Obs.
$(\delta_1)/(-\delta_1)$	= 35616.71 ...16.73
$(-\delta)/(\delta)$	= ...68.40 ...69.186 Cd.,

but they are No. 8 in the satelloid list. P. gives 35622.11, 5.38 larger. It may be 2δ on s7, shift=5.32.

The first S_2 by W. ($\lambda=5316.87$) is marked "i" on the supposition that it is the same as 5317.2 by Bl., which is doubtful. The last four are a successive set by E. V.

	Obs.
$(2\delta)/(\delta)$	= 17543.16 ...43.03 P.
$(5\delta_1)/0$	= .. 53.29 ...52.5 E. V.

S(3.m) (cont.).

S(4.m) (cont.).

$m=8$.

Collaterals show that $[S_1]$ should be about .23 less. Thus

	Obs.
$(-\delta)/(-2\delta_1) = 37202.43$...02.426
$(2\delta)/(-9\delta_1) = 37149.40$...49.48 D.
$(10\delta_1)/(-11\delta_1) = 37129.15$...29.33 D.

The last is $(2\delta_1)/(-2\delta_1)$ on the second, but see D(3.8).

$m=9$.

The calc. S_1 differs from the obs. by 2.72 or the persistent satelloid 6 μ . The separations are taken from []. With the observed line

	Obs.
$(3\delta_1)/(-3\delta_1) = 38228.89$...29 D.

$m=10$.

$m=11$.

The intensity for the 72 $\frac{3}{4}\delta$ is that for it and a near line combined.

Collaterals.

	Obs.
$(3\delta_1)/(3\delta_1) = 19101.11$...01.6 E. V.
$(6\delta_1)/(3\delta_1) = 19088.35$...88.1 Stk.
$(-6\delta_1)/(-3\delta_1) = 136.77$...36.7 Stk.

The last S_2 has reliable measure, and corrects $[S_1]$ by .28, and this simultaneously alters the $d\lambda$ for the others to 0, 0, .23, -.09, 00. This excludes the 70 $\frac{3}{4}$.

$(-5\delta_1)/(-5\delta_1) = 20223.51$ (or .79)	Obs. ...23.8 E. V.
---	--------------------

If $[S_1]$ be taken .50 less the three reliably measured lines give separations respectively with $d\lambda = .00, -.01, -.01$, but E. V.'s require -.2.

The two reliable measures for the 68, 70 $\frac{3}{4}$ lines differ by 50.34 compared with $1251.84 - 1201.44 = 50.40$. Accepting them as true, S_2 corrects E. V.'s S_1 by -.68 ($d\lambda = .14$). Also reduces that for 71 $\frac{3}{4}$ to .1.

Table of Observed Collaterals in Oun Multiples.

m .	S(2.m).	S(3.m).	S(4.m).
1.	$\pm 1/\pm 1$		
2.	$-1/+1$; $\pm 1/\mp 2$ $-3/3$; $-4/2$		
3.	$\pm 2/\mp 1$	$\pm 1/\mp 2$	
4.	$-4/-4$	$\left. \begin{array}{l} 2/-6 \\ -2/-2 \end{array} \right\} \text{rel } 4/-4$ $1/0$; $-3/4$	
5.	$-1/1$; $2/2$ $-3/3$	$-1/1$; $-2/-2$...
6.	$4/-4$
7.	$-4/-4$	$-4/4$; $1/-1$	$8/4$; $5/0$
8.	...	$-4/-2$ $8/-9$; $10/-11$	$3/3$; $\pm 6/\pm 3$
9.	$1/1$; $8/8$	$3/-3$ $3 \text{ A } 2$	$-5/-5$

TABLE IV.— $e.S^2(2.m)$.

$$e=20612.06.$$

<i>m.</i>	<i>l.</i>	<i>n.</i>	<i>v.</i>	$d\lambda$.					
1.	3 i	-36883.272		0	6.	[61968.88]			
	1	-27795.3	9088.0	-.18 69 $\frac{1}{4}$	3	71407.86	9439.0	.01	71 $\frac{1}{2}$
2 <i>y</i>	2	725.185	158.09	.01 69 $\frac{3}{4}$	1	653.8	685.0	.05	73 $\frac{1}{2}$
	1	688.3	195.0	-.36 70	7.	[64236.0]			
	1	617.2	266.1	-.4 70 $\frac{1}{2}$	0	73399.9	9163.9	.12	69 $\frac{3}{4}$
	3	514.350	368.92	-.01 71 $\frac{1}{4}$	2	458.71	222.7	.05	70 $\frac{1}{4}$
4 <i>y</i>	8 ii	477.259	406.01	.00 71 $\frac{1}{2}$	2	501.3	265.3	.04	70 $\frac{1}{2}$
	1	052.3	831.0	-.2 γ		674.55	438.5	.01	71 $\frac{1}{4}$
2.		[14492.10]			? 1	74060.30	824.3	.09	γ
	1	24545.0	9052.9	-.3 69	8.	[65773.92]			
-5 <i>y</i>	4 ii	611.783	9119.68	.03 α	0	72.2		.04	
	3	649.180	157.08	.00 69 $\frac{3}{4}$	* 3	74861.5	9089.3	.05	69 $\frac{1}{4}$
-2 <i>y</i>	1	24001.339	509.24	-.02 72 $\frac{1}{4}$	3	895.1	122.9	.01	α
	1	005.7	513.6	.3 72 $\frac{1}{4}$	1	928.8	156.6	.00	69 $\frac{3}{4}$
5 <i>y</i>	1	112.735	618.67	.02 73	4	75142.8	370.6	.03	71 $\frac{1}{4}$
3 <i>y</i>	2 ii	145.566	653.46	.01 73 $\frac{1}{4}$	3 <i>n</i>	386.4	614.2	.04	73
8 <i>y</i>	1	147.635	655.53	.02 73 $\frac{1}{4}$	3	568.6	896.4	.08	75
-3 <i>y</i>	1	178.463	686.36	.02 73 $\frac{1}{2}$	9.	[66865.22]			
4 <i>y</i>	4 ii	252.537	760.44	.00 74	1	76132.5	9267.3	.07	70 $\frac{1}{2}$
3.	0 iii	40968.66		-.04	1	266.0	400.8	.05	71 $\frac{1}{2}$
	1 ii	50478.29	9509.63	.02 72 $\frac{1}{4}$	2	593.1	727.9	.08	73 $\frac{3}{4}$
-7 <i>y</i>	2 <i>m</i> i *	617.53	648.87	.00 73 $\frac{1}{4}$	1	799.0	933.9	.04	75 $\frac{1}{4}$
-2 <i>y</i>	2 <i>m</i>	690.65	722.00	0 73 $\frac{3}{4}$	10.	[67667.61]			
4.		[52418.67]			4	69.52		.04	
	*	9830		0 γ	0	77077.2	9407.7	.03	71 $\frac{1}{2}$
5.		* [58424.60]				106.9	437.4	.04	71 $\frac{3}{4}$
	0	67444.5	9019.4	.06 68 $\frac{3}{4}$	0	220.1	550.6	.08	72 $\frac{1}{2}$
	2	755.3	330.7	.06 β	0	429.3	759.8	.02	74
	1	870.2	445.6	.1 71 $\frac{3}{4}$					
	2	68150.0	725.4	.05 73 $\frac{3}{4}$					
	3	222.1	797.5	.07 74 $\frac{1}{4}$					

* See *nhv* list.

1. 2710.454; 3596.8 Stk.; 3605.804; ...10.7; ...20.0 Stk.; ...33.435; ...38.340; ...95.6.—2. 4246.1 Stk.; ...33.985; ...27.290; 4196.684; ...65.264; ...64.6; 46.024; ...40.385; .. 40.182; ...34.750; ...22.121.—3. (2440.15; 1980.40; ...74.95; ...72.10) D.—5. 1482.7; ...75.9; 73.4; ...67.35 McL.; ...65.8.—6. 1400.406 P.; 1395.6.—7. 1362.4; ...61.307 P.; ...60.52 McL.; ...57.321 P.; ...50.251 P.—8. 1520.4; 1335.8; ...35.2; ...34.6; ...30.8; ...26.5; ...23.3.—9. 1313.5; ...11.2; ...05.6; ...02.1.—10. 1477.770 P.; 1297.8; ...96.9; ...95.4; ...91.5.—11. 1291.5.

As in the $S(2.m)$ lines all contain the p^2 term, the presence of satelloids may be not unexpected. It has been found that in Cu linkages exact link values frequently go to main-line satelloids, so that a similar effect should be looked for here. This can only be tested where we have very accurate measures. Where these have been found, the suggested y multiples are entered in the first column (m) and the residual errors in the $d\lambda$ column.

Notes.

$m=3$. 40968.0 is calculated from C.'s 61580. If we use P.'s 61578.06, giving 40966.00, the observed $d\lambda = .15$ is probably $> O.E.$ This would seem to establish C.'s as a real value, satelloidal 2.71 to P.'s.

As $2h\nu$ with exact ν , without satelloids

$$1, 2 \ (25310.274 + .08) \quad 50620.70 \quad \mathbf{9652.04} \quad .01 \quad 73\frac{1}{2}$$

$m=4$. No representatives for $e.S_1$ or $e.S_2$ have been noted. But we do find $u.S_1$ and $e.S_1.u$. I find the neutral u link, calculated from a possible $s1$ (an allocation not published), and tested on a long list of neutral lines, to be 14819.4. With this

$$\begin{array}{ll} \text{Obs.} & \\ u.S_1(4) = 73030.75 - u = 58211.3 & \dots 06 \text{ (Ly.)} \\ e.S_1(4).u = 52418.67 + u = 67338.1 & \dots 40.1 \quad d\lambda = -.04 \end{array}$$

As a possible $2h\nu$ effect

$$\begin{array}{ll} 2 \times 31124.47 = (62248.94) & \text{gives } \mathbf{9830.1} \gamma \quad d\lambda = .00 \\ \lambda = 2, 3211.98 \text{ P.} & 2 \text{ iii } 3212.0 \text{ Bl.} \end{array}$$

$m=5$. The $72\frac{3}{4}\delta$ line, 1467.35, is McL.'s measure ($C = \dots 7.5$). This also shows 9334.4 forwards. McL. allocates this to a doubly ionized line iii d^3p^3 .

$$2h\nu \ 2(29210.9 + 1.4) = e.S_15 \quad d\lambda = .1$$

$m=6$. 71407 is also S_2^23 .

$m=8$. For the first S_2 there is a $2h\nu$ representative which gives nearly an exact ν , viz., $2 \text{ i}, 2 \times 37428.9 = 74857.8. \mathbf{9085.6}$.

$m=9$. The first separation 9267.3 may be a representative of the 9268.7 appearing with the S_12 list in §1.

TABLE V.— P^2m .

$$s_1 = 149519.64.$$

$$s1 = 63.26.$$

$$s_2 = 56920.18.$$

92599.46.

$$s_2 = 14.865.$$

$$s_3 = 30444.3.$$

26475.9.

$$s_3 = 5.8147.$$

$$p_1(m) = 4R / \{m + .236030 - .103608/m\}^2.$$

$p_1 =$	$m.$	$I.$	$n.$	$v.$	$d\lambda.$				
						$P(1.m).$		$P(2.m).$	
						see S1.		see —S2.	
						9.6708.			
						3. 1 * 106712 ± 5 [...16]	1	14116.93	0
						* 0 103928 2784 0 68½	1	11394 2723	67
						1 864 2848 0 70	1	11363 2754	67½
						2 605 3107 0 76	1	11319 2798	68½
							1	11077 3040	γ
						4.2625.			
						4. * [124768]	1 i	32169.257	0
							1	30971.558	0 67½
							½	73.96	
						2.2435.			
						5. [133384]	1 i	49784.65	6
							0	148.5	636.1 —.03 69
							* 1 i	096.52	688.13 .1 γ

P(3.m).									
1·3936.									
6.	1 i	19101·6		3		1 ii	45550·67	} §	
	2n i	18741·4	360·2	0	66½	0 ii	606	} †	
	3	712·3	389·3	0	71½	* 0 ii	230·88	375·2†	0 69½
	3 i	699·7	401·9	0	74	0	163·00	387·67§	0 71½
	1n	678·4	423·2	-·2	77¾				
·8445.									
7.	3	22034·79		·09		* 0n i	48482·91	}	
	2 ii	21794·6	240·2	·08	α	* 0 i	521·50	}	
	3	780·84	253·95	·02	73½	0 iii	279·70	241·80	·01 70½

•5718.

$$\begin{array}{r} 8. \text{ 3 ii } 23941 \cdot 770 \} \\ \quad 1 \quad 983 \cdot 644 \} \\ \quad 1n \quad 798 \cdot 9 \end{array}$$

$P(1, m)$. 3. 937.1; 962.2; 962.8; 965.2.

P(2.m). 3. 7081.96 St.; (8774; ...98; ...88.32; 9025) McL. —

4. 3107-659; 3327-840; ...7-59 Od.—5. (2451-16: ...90-0: ...93-23) D.—

6. 2194·67; ...92; 2210·19; ...13·51) D.—7. (2061·92; ...60·28; ...70·60) D.

P(3.m). 6. 5223·8; 5334·3; ...42·6 P.; ...46·3; ...52·4. — 7. 4537·01 P.; 4587·1; ...89·91 P. — 8. 4175·628; ...68·337; 4200·8.

Notes.

$m=3$.—In P(2.3) the correct ν are 2721.03 ; 53.06 ; 95.65 ; 3041.67. The last three P_2 have similar linkages, viz. :—

	9828.1	1	20905.1	9120.8	3 iii	30025.9 Bl.
1, 11077	9121.3	1 ii	20198.32	9826.6	↑	9332.02 ↓
	9330.5	1 iii	20407.52	9122.82	1	29530.34
	9829.4	1 iii	21148.01			
11319	9124	2n	20443.07	11363	9122.7	1 ii 20485.7
	9331	1 iii	20650.43			

In P(1.3) there is also a possible $2h\nu$ representative

$$2 \times 51040.00 \text{ iii } D = 103889.0 \quad 2836\gamma \quad d\lambda = .04.$$

$m=4$. There is a long set of successive lines, only observed by Bl., and all of class E2, which fit in for various P_2 lines :—

1.	1	3243.7	30820.1	1349.2	$d\lambda = .1$	76 δ
2.	1	43.9	843.9	25.4	0	74 $\frac{3}{4}$
3.	1	39.4	861.0	08.3	— .13	73 $\frac{3}{4}$
4.	1	38.5	869.6	1299.7	— .2	73 $\frac{1}{4}$
5.	2	35.3	900.1	69.2	.1	71 $\frac{3}{4}$
6.	2	30.7	944.1	25.2	— .1	69 $\frac{1}{4}$
7.	1	25.9	990.2	1179.1	— .06	66 $\frac{3}{4}$
8.	1	24.0	31008.4	60.0	— .07	65 $\frac{3}{4}$

with, possibly, a few others of larger multiples. The class iii points to the supposition that these are not normal lines, but accidentals formed by the high excitation. Many show similar links. Thus 1, +9123.1 ; 2, +9121.8 ; —9122.0 ; 3, +9121, —9823.9 ; 4, —9828.0 ; 5, —9829.4 ; 7, —9121.2, +9828.1.

The following collateral coincidences may be noted :—

	Obs.
$(2\delta_1)P(1.4)(-\delta) = 124624.5$	1 ...22.1
$(\delta)P(2.4)(-\delta_1) = 32105.54$	1 iii ...05.8 Bl.
$(\delta_1)P(2.4)(-\delta_1) = 32150.13$	3 iii ...49.2 Bl.

$m=5$. The formula $P_1(2.5)$ is 40794.58. Denoting this by (P).

		Obs.	
$[P](-\delta_1)=40785.61=X$	1 i ... 4.65 D.	$d\lambda=-.06$	
$(2\delta_1)X(-2\delta_1)=51.40$	0 iii ... 51.4 D.	$d\lambda=0$	
$(-2\delta_1)X(\delta_1)=40817.58$	0 ii ... 18.29 D.	$d\lambda=.04$	
$(-3\delta_1)X(-\delta_1)=27.942$	2 ii ... 27.96 D.	$d\lambda=0$	

$$* 3, 2 \times 20048.2 \text{ E. V.} = P_2.$$

40784 has a curious linkage set, viz.,

1 ii 40784.65	9331.37	6 ii 50116.02	* 2, 2×25059.006 , exact β .
	↓ 9832.88		
6 41286.73	9330.80	2 ii 50617.53	* 3, 2×25308.9 E. V.
	↑ 9126.22		
0 ii 41491.31	9330.80	0 i 50821.79	
	↓ 9830.48		
1 ii 41988.81	9332.8	4 i 51321.79	* 1, 2×25660.733
	↑ 9122.8		
0 42199	↑		

$m=6$. The formula value for $P(2.6)$ is 45578.90, which is the mean of the two bracketed lines in the list. These are separated by 55.3. A displacement δ/δ shifts 59.46 - 4.01 = 55.45. They therefore suggest $(\pm 2\delta_1)/(\pm 2\delta_1)$. Taking the reliable measure 45550.67 as $(2\delta_1)P(2\delta_1)$ gives $P=45578.39$, which reproduces the formula value ($d\lambda=.02$), but no P_2 lines corresponding to this have been noted. 45163 is an arc line and $D_{33}^3 8$, and is probably a coincidence.

$$* 2 \text{ iii } 2 \times 22615.5 = P_2 6.$$

The $P(3.m)$ now come into view. The calculated P_1 is 45578.39 - 26475.90 - 19102.49, obs. by E.V ... 1.6.

$m=7$. Again we find the formula value of 48509.14 disrupted into two, viz.,

	Obs.
$(2\delta_1)P(\delta)=48482.78$...82.91
$(-\delta_1)P(-3\delta_1)=...521.47$...21.50

with two $2h\nu$. * $2 \times 24241.07 = P_1$; $2 \times 24261.843 = P_1$.

The calculated for P(3.7) is 22035.24, for which we find three close lines.

1 iii 22032.698 St. 2 09 3, ...4.79 P. 2 82 2, ...7.61 P.

which appear satelloidally connected. The α separation for p_7 is 239.76 and $p_2 7 = 880.5$.

$m=8$. The formula value for P(3.8), 23957.82, is not observed, but two near lines on either side fit as collaterals:—

	Obs.
$(3\delta_1)P(2\delta_1)=23941.5$...41.770
$(-\delta)P(\delta)=...83.3$...83.644

These are very reliable measures with separation = 41.874. The two sets of displacements give $(23.359 + 2.287) + (17.444 - 1.143) = 41.847$, or $d\lambda = .005$ on two lines, a remarkably close agreement. The 23798 may be a P_2 representative to an intermediate line. The doublet separations corresponding to 69δ , 74δ are 160.76, 172.65.

pp Combinations.

In these tables wave numbers in the same horizontal line refer to the same $p(2)$; in the same column to various $p_2 3$ or $p_2 4$; thus 55302 is $\alpha p_2 - \gamma p_3$, αp , etc., denoting the p_2 depending on the $69\frac{1}{2}\delta$ displacement, etc. To save space, however, a given column is not confined to the same p_2 . Over each wave number are placed (1) the separation from the corresponding p_2 on the left, (2) the displacement involved as a multiple of δ , and (3) the O—E $d\lambda$. The λ are given below, each column in order. Examples for the $(69\frac{1}{4})p_2 2$ are also given. It will be noticed that no $p_1 2 - p_1 m$ are observed.

	$p_2 \cdots p_4$		
$p_2 - p_1 4$	1214.5	$68\frac{3}{4}$.01
$p_1 2[67273.42]$	2, 66058.9	—	—
9086.59	1217.2	69	.05
$(69\frac{1}{4})\delta[76360.01]$	4, 75142.8 ⁽¹⁾	1, 75086.3 ⁽²⁾	.02
9121.9	1252.5	$70\frac{3}{4}$.01
$\alpha p_2[76395.30]$	4, 75142.8 ⁽¹⁾	1, 75086.3 ⁽²⁾	.04
9333.4	1220.4	69	.01
$\beta p_2[77606.8]$	2n, 75386.4	—	—
9833.5 (.06)	—	—	—
γp_2 2, 77106.9	—	—	—

1296.9; 1513.8, 1330.8, ...1326.5; 1331.8, ...

(1), (2) Necessarily closely the same. Also (1) is $e. S_2 8$.

*p*2—*p*3.

<i>p</i> 2— <i>p</i> 1,3	2825.99 <i>α</i> —.07	2846.86 70 —.1	2915.8 71½ .03	3051.31 74¾ —.09
<i>p</i> 1[49221.09]	1 i 46395.10	3 iii 46374.25	0 i 46305.3	0 ii 46170.78
9086.59 69½	—	2870.4 70½ 0	—	—
(69½δ)[58307.68]	—	3 55437.3	—	—
9121.9 <i>α</i>	2807.2 69 .02	—	—	3040.6 γ .04
<i>α</i> <i>p</i> 2[58343.0]	1 55535.8 (1)	—	—	2 55302.4
9333.4 β	—	2879.6 70¾ —.06	2956.9 71¾ .04	3018.7 74 .05
β <i>p</i> 2[58554.5]	—	7 55674.9 *	9 55597.6 (2)	1 55535.8 (1)
9829.7 γ	—	2870.1 70½ 0	—	—
γ <i>p</i> 2[59051.8]	—	1 56181.7	—	—

2154.72, 1800.7; 2155.69, 1803.9, 1796.2, 1780.0; 2158.9, 1798.7; 2165.19, 1808.3, 1800.7. The lines in *R.A.* are by *Ly*.

(1) These are necessarily very close.

(2) This belongs also to a set parallel to *S*1(*Hg*I), viz.:—1531—*S*1. Also this and 55674 should probably be excluded as too intense, in spite of numerical agreement, or they may be covered by stronger lines.

The latter has a *2hν* representative, but it probably belongs to some other allocation.

TABLE VI.— D^2 ; $(8\Delta_\alpha)$.

92024.34	$p_12 = 30.557$	
42803.25	$p_13 = 9.6708$	Sep. = 49221.09
24750.92	$p_14 = 4.2625$	„ = 18052.33
$d_1m = 4R/\{m + .811818 + .008086/m\}^2$.		

$d_1m -$ m	I.	n .	ν .	$d\lambda$.						
		$D(2.m)$.					$D(3.m)$.			
		52.768; $d_2 = 53.99$.								
1.	8 ii	{	-42463.90	0		[-91684]				
	2 i	{	-40435.78	2028.12	0	9 $\frac{1}{2}$	1 n	-89645	2038	
	1 n		-33200.14	9263.76	.08	70 $\frac{1}{2}$				
		14.246; $d_2 = 14.439$.								
2.	1 i	{	36192.88	0		3	{	-13028.21		
	4 ii	{	694.5	501.63	0	8 $\frac{3}{4}$	1	-(12526.55)	501.66	
	1 i		45533.86	9340.98	$\beta + 7.57$	1		-10296	2732.2	.5 67 $\frac{1}{4}$
	4 i		632.36	9439.48	0	71 $\frac{3}{4}$	2	-10084	2944.2	.8 72 $\frac{1}{4}$
	0 i		46029.85	9863.97	$\gamma + 7.24$	3		-9784.9	2741.6	.7 67 $\frac{1}{2}$
						4	{	-9664.8	2861.7	.2 70 $\frac{1}{4}$
						6		-9634.1	2892.4	.7 β
		5.7307; $d_2 = 5.795$.								
3.	1	{	61648.5	0			{	[12427.41]		
			[61873.18	224.7	0	9 $\frac{3}{4}$		[12652.09]	224.6	
	1		70700.35	9051.5	.00	69	2	15330.54	2903.13	-.3 71 $\frac{1}{4}$
	0		736.4	9087.9	.02	69 $\frac{1}{4}$				
	2		71407.86	9759.3	.02	74				
D_{21}	0		957.2	9084.0	-.05	60 $\frac{1}{4}$				
		2.851								
4.	0	{	72987.4			3	{	23768.32		
			[73092.22]	104.8	-.02	9 $\frac{1}{4}$	1.	23870.5	102.2	.1 9
	1		82182.8	9195.4	.04	70	1	26703.64	2935.32	-.10 72
	4		82250.4	9263.0	.003	70 $\frac{1}{2}$	1 ii	712.69	2944.37	-.11 72 $\frac{1}{4}$
							1	767.83	2999.51	-.11 73 $\frac{1}{2}$
		1.6226								
5.	1 n	{	78982.7			3 ii	{	29764.23		
			[79043.10]	60.4	0	9 $\frac{1}{4}$	1	29827.86	63.63	.03 9 $\frac{1}{4}$
	0		88778.4	9795.7	.02	74	1 iii	32527.8*	2763.7	0 68
							1 iii	549.0	2784.8	0 68 $\frac{1}{2}$
							2 iii	654.3	2890.1	.1 β
							3 i	709.60	2945.4	0 72 $\frac{1}{4}$
		1.0057								
6.		{	[82534.86]				{	[33313.77]		
	*		[...73.22]	[38.36]		9 $\frac{1}{2}$		[52.13]		
	1		91650.6	9115.7	.07	α	3 i	36195.35	2831.58	-.04 70 $\frac{1}{4}$
							1	355.15	3041.38	.02, γ

TABLE VI.— D^2 ; $(8\Delta_a)$ (cont.).

$\cdot 6669$	$D(4.m).$							
7.				7.				
	$\left\{ \begin{array}{l} [17539\cdot 1] \\ [564\cdot 4] \end{array} \right.$				$\left\{ \begin{array}{l} [35591\cdot 39] \\ 1\text{ i } 616\ 73 \\ 2\text{ ii } 38323\cdot 04 \\ 2\text{ i } 472\cdot 99 \\ 2\text{ i } 601\cdot 62 \\ 1\text{ i } 631\cdot 47 \end{array} \right.$			
						2731·65	$\cdot 00$	$67\frac{1}{4}$
						2881·60	$\cdot 04$	$70\frac{3}{4}$
						3010·24	$\cdot 06$	$73\frac{3}{4}$
						3040·08	$\cdot 1$	γ
				D_{21}	$\left\{ \begin{array}{l} 3\text{ ii } 326\cdot 98 \\ 0\text{ ii } 518\ 05 \end{array} \right.$	2710·25	$\cdot 01$	$66\frac{3}{4}$
						2901·32	$\cdot 07$	$71\frac{1}{4}$
$\cdot 4648$				8.	$2\text{ i } 37149\cdot 38$			
8.	$[19097\cdot 15]$				$[53\cdot 49]$	4·01	$\cdot 01$	9
	$1\text{ i } 101\cdot 6$							
	$20236\cdot 4$	1169·3	0	$66\frac{1}{4}$	$1\text{ i } 39965\cdot 73$	2816·25	$\cdot 04$	$69\frac{1}{4}$
	$2\text{ i } 348\cdot 9$	1251·7	$\cdot 03$	$70\frac{3}{4}$	$1\text{ i } 998\ 09$	2848·61	$\cdot 02$	70
	$1\text{ i } 390\cdot 609$	1293·46	$\cdot 06$	73	$1\text{ i } 40096\cdot 52$	2947·04	$\cdot 00$	$72\frac{1}{4}$
					$0\text{ ii } 191\cdot 62$	3042·14	$\cdot 03$	γ

$D(2.m).$ 1. 2354·216; 2472·31 D.; 3011·17 K.—2. (2762·25; ...24·4) E. H.; (2195·48; ...90·74; ...71·82) D.—3. 1622·1 Bl.; 1414·427 P.; ...13·7; ...00·416 P.; ...09·3.—4. 1370·1; 1216·8; ...15·8.—5. 1266·1; 1126·4.—6. 1091·1.

$D(3.m).$ 1. 1115·5.—2. 7673 McL.; 7944·66 P.; (9710; 9914; 10217; 10344; 10377) McL.—3. 6521·13 P.—4. 4206·100; 4188·2 Stk.; 3743·747; ...42·480; ...34·770.—5. 3358·775; ...51·61 St.; (3073·4; ...71·4; ...61·5) Bl.; ...53·32 P.—6. 2761·971; ...49·83 P.—7. 2806·844; 2608·618; (2598·45; ...89·79; ...87·79; 2608·35; 2595·41) D.—8. (2691·03; ...01·39) D.; 2499·366; (...93·23; ...88·58; 87·33) D.

$D(4.m).$ 8. 5233·8; 4933·0; .. 13·0; ...02·853.

$m=1$ (see text). The neutral e linked line to the corrected $D_{11}(3\cdot 1) = -89657$ is found. Thus

Obs.

$$-89657 + 20612 = 69045 \quad \dots 46\cdot 5 \quad 2, 1448\cdot 3$$

The αD_2 should be at 33342·10. It is just possible this may be indicated by Bl. λ , 1 i 5994, 16678, $d\lambda=2$ as $2h\nu$.

$m=2$. For D_{12} S. gives a value 2·46 larger. The measures of E. H. are inserted because they give the exact value of γ , 9439·49 and also a satellite separation which is due to an exact own multiple $8\frac{3}{4}\delta$ within O.E. calc. $\sigma=502\cdot 03$, $d\lambda=0\cdot 03$. The first and third ν are $17y=7\cdot 70$ and $16y=7\cdot 25$ in excess, and are entered only as suggesting the presence of the satelloidal effect.

In the D(3.2) the three last entered as D_{21} are too strong. They are probably only coincidences. $m=2, 3$ are in the infra-red, with only few observations, and none in the spark spectrum. Little weight, therefore, can be given to these allocations.

$m=3$. No line is observed for the calculated D_{11} , but the calc. (61873) gives an exact $9\frac{3}{4}\delta$ displacement with $\sigma=224.78$. Also d_12, d_3 combinations sustain the allocations with a $2h\nu$ representative. Although D_{11} is not seen, the forbidden D_{21} is. The vanishing of D_{11} suggests that it has been disrupted into collaterals. One such is given by Bl. at 1, 1617.5, 61820.0 which is $(\delta_1)D_{11}(-\delta)$, $d\lambda = .005$. For intensity comparison with the others, the intensity of 70700 is given as 1, that of Bl., instead of 9 by P., as his excitation was more comparable. In the original allocation the measures of Bl. and Ly 1414.4 and 1400.4, were used giving separations 9052.8, 9760.8. It is striking to see how, with Paschen's good measures, the practically exact values 9051.41, 9758.61 result. But they are also equally good $S_2(2.3)$ with 9121.99, 9829.80.

$m=4$. In D(3.4) the D_{12} calculated from D(2.4) is 2.00 too small, possibly the error is in the latter. If the observed is a one own collateral (shift = 2.85), it should be .85 larger ($d\lambda = -.1$) when the three D_2 separations from the accurately measured lines all become exact.

The $2h\nu$ basis affords two extra D_2 , viz.,

$$2 \times 41212.52 \text{ D } 2 \text{ iii} = 82425.04 \quad \mathbf{9437.6} \quad .02 \quad 71\frac{1}{2}$$

$$2 \times 41373.86 \text{ D } 1 \text{ i} = 82747.72 \quad \mathbf{9760.3} \quad .02 \quad 74$$

$m=5$. The satellite separation for $9\frac{1}{4}\delta$ is 60.09.

The $D_{12}(3.5)$ calculated from D(2.5) is 2.62 too large. The observed gives the exact D_2 separations shown, but the calculated 29761.61 gives also close values with the following:—

$$\text{Bl. } 1 \text{ iii } 3059.6 \quad 32674.5 \quad \mathbf{2912.9} \quad 0 \quad 71\frac{1}{2}$$

$$\text{.. } 1 \text{ iii } 53.7 \quad 737.7 \quad \mathbf{2976.1} \quad .1 \quad 73$$

$$\text{P. } 3 \text{ ii } 45.56 \quad 825.16 \quad \mathbf{3063.55} \quad -.04 \quad 74\frac{1}{2}$$

The satellite separation of 63.63 is an extra $2\delta_1$ displacement on the D(2.5) value, i. e., it is due to $9\frac{3}{4}\delta$.

There is a line near D_{11} at 1, iii 29832.42, whilst Cd. gives a single line at the mean of these two. The separation is 4.56, and is possibly a satelloidal $10y$ with Cd. at $5y$.

$$* 2 \times 16263.79 = 32527.58 = D_{22}.$$

$m=6$. The non-observed $D_{11}(2.6)$ is sustained by a $2h\nu$ effect.

$$2 \times 41286.73 D., 0. = 82573.46$$

$m=7$.—The formula value for D_{11} is 35616.23, obs. ...6.73.

dd Combinations.

Obs.

$d_2 2 - d_2 3$	[25453.1]	...52.31	1, 3927.81	$d\lambda = .1$
$d_1 2 - d_2 3$	[24954.6]	...53.85	3 ii 4006.27	$d\lambda = .12$
$d_1 2 - d_1 3$	[25779.19]	...80.5	1, 3970.3	$d\lambda = .2$

No $d2 - d(4, 5)$.

$$d1 - d2.$$

Obs.

$d_1 - d_2$	[76628.66]	...34.2 *	1, 1304.9	$d\lambda = -.09$
$d_1 - d_1$	[77130.29]	$(\pm \delta_1)/(\pm 2.1\delta)$		

The observed $d_1 d_2$ shows an exact $2h\nu$ effect, viz., $2 \times 38317, 2609 D.$

There is no direct obs. for 77130, but two exact collaterals are found.

$(+\delta_1)/(2\delta_1)$ shifts $52.77 - 28.49 = 24.28$. Thus

Obs.

$(\delta_1) [] (2\delta_1)$	$= 77106.01 *$...06.9	2, 1296.9
$(-\delta_1) [] (-2\delta_1)$	$= ...54.57 *$...54.5	0, 1296.1

The mean of the two is the exact $d_1 d_1$. The first shows a $2h\nu$ effect and the second a $3h\nu$, viz. :—

2×38555.19	1 iii 2592.91 D.	$d\lambda = .1$	on $d_1 d_1$
3×25718.999	1, 3887.079	$d\lambda = .02$	„ „

If both these are real relations they must give within their O.E. lines which differ by an exact $2 \times (\delta_1)/(2\delta_1)$, or

48.56. With O.E. $d\lambda_1 d\lambda_2$, their W.N. are less by $14.86 d\lambda_1$, $6.60 d\lambda_2$. The difference is therefore

$$(\dots 57.0 - 19.8 d\lambda_2) - (\dots 10.38 - 29.7 d\lambda) \\ = 46.6 + 29.7 d\lambda_1 - 19.8 d\lambda_2.$$

Thus $29.7 d\lambda_1 - 19.6 d\lambda_2 = 2$.

As $d\lambda_1 = .1$, $d\lambda_2 = -.05$ would produce 4, we may consider the condition met.

$$d_1 - d_2 \quad [78656.78] \quad \begin{matrix} \text{Obs.} \\ (\pm \delta_1) / (\mp 3\delta_1) \end{matrix}$$

No direct obs., but the two collaterals named are found.

$\delta_1 / -3\delta_1$ shifts $53.99 + 3 \times 14.439 = 97.30$. Thus

$$\begin{matrix} & & \text{Obs.} \\ (\delta_1) [] (-3\delta_1) = 78559.48 * & \dots 560.8 & 0, 1272.9 & d\lambda = .02 \\ (-\delta_1) [] (3\delta_1) = 78754.08 & \dots 752.6 & 4, 1269.8 & d\lambda = .04 \end{matrix}$$

The first shows both $2h\nu$, and $3h\nu$ effects, viz. :—

$$\begin{matrix} 2 \times (39279.4 \pm .8) & \text{ii} & 2545.1 D, & d\lambda = .01 \text{ on } d\lambda \\ 3 \times 26187.199 & 1. & 3817.571 & ,, -.1 \end{matrix}$$

Here, if both are real, they must give the same value within O.E. Hence,

$$\dots 58.8 - 15.4 d\lambda_1 = \dots 61.60 - 6.85 d\lambda_2$$

$$\text{or} \quad -15.4 d\lambda_1 + 6.85 d\lambda_2 = 2.8$$

With $d\lambda_2 = .05$ this requires $d\lambda_1 = -.16$, and the connexion is perhaps just possible.

$$d1 - d3.$$

We get only displaced representatives for each possible combination. As, however, the own shift on the $d3$ is about 6, which corresponds to $d\lambda = .06$ on these high wave numbers, we can have no certainty within about one own on $d3$. In the following list the calculated $d - d$ are in [].

$$\begin{matrix} & & \text{Obs.} \\ d_1 - d_2 & (\delta_1) [102084.3] (\delta_1) = 102037.3 * & \dots 041 & 1, 980.0 \\ & (-\delta_1) [] (\delta) = 102113.9 & \dots 114 & 4, 979.3 \\ d_1 - d_1 & (-\delta_1) [102309] (-3\delta_1) = 102344 & \dots 344 & 7, 977.1 \\ d_2 - d_2 & (2\delta_1) [104112] (2\delta_1) = 104016.1 & \dots 015 & 1, 961.4 \\ d_2 - d_1 & (-\delta_1) [104337] (-\delta_1) = 104385.3 * & \dots 384 & 4, 958.0 \end{matrix}$$

The following $n\hbar\nu$ are found:—

$$0\text{ i } 1958\cdot57, \quad 2 \times 51040\cdot98 = 102081\cdot96 \quad \text{gives } d_1 - d_2$$

$$1\text{ i } 2873\cdot243, \quad 3 \times 34793\cdot693 = 104381\cdot08 \quad \text{gives } (-\delta_1)d_2d_1(-\delta_1)$$

TABLE VII.— F^2 ; $(9\Delta\alpha)$.

$$d_11 = 132460\cdot12, \quad \sigma = 2028\cdot12, \quad d_1- = 52\cdot768; \quad d_2- = 53\cdot986.$$

$$d_12 = 55330\cdot09, \quad \sigma = 502\cdot02, \quad d_1- = 14\cdot246; \quad d_2- = 14\cdot439.$$

$$d_13 = 30151\cdot2, \quad \sigma = 224\cdot6, \quad d_1- = 5\cdot734; \quad d_3- = 5\cdot795.$$

$$f_2m = 4R/\{m + \cdot887110 + \cdot015588m\}^2.$$

$F(1.m).$

$F(2.m).$

$$f_2- = 13\cdot093; \quad af_2- = 13\cdot048; \quad f_1- = 13\cdot024; \quad cf- = 12\cdot983.$$

2.	2	1n *	80153·9			9 δ_1 gives	117·68
	a	1	276·1	122·2		10 δ_1 „	130·75
F_{11}	b	1 *	340·6	186·7		14 δ_1 „	182·80
	c	1n *	450·5	296·6		23 δ_1 „	299·84
		1	82182·8	2028·9			

$$f_1- = 5\cdot365; \quad f_2- = 4\cdot395.$$

3.	1	103498		1	26375·42	0
	2	605	107	1	477·683	19 δ_1
	1	105530	2032	1	[877·61]?	F_{22}
				1	980·22	F_{21}

$$f- = 2\cdot718.$$

4.				4 i	(36952·74)	
				5 i	992·23	(39·51)
				3 ii	(37459·32)	(506·60)
				1 ii?	494·02	501·80

$F(3.m).$

$$f- = 1\cdot554.$$

5.	1 iii	17515·3	(25178·5)	3 i	42693·84	—·51
				4 i	(733·48)	(39·64)
	2 ii	17732·788	217·5	5 i	43194·63	500·8

$$f- = \cdot972.$$

6.	1 iii	20910·7	(25178·2)	0n i	46111 ±	[... 087·77]	1
		— — —	— — —	1 i	(148·40)	(38 ±)	
	3	21136·6	225·9	1 i	612·48	501	

$$f- = \cdot747.$$

7.	1 iii	23104·091	(23178·29)	0 iii	48379·7	[... 81·53]	—·09
	1	23228·2	224·1				
8.		[24600]		0 iii	49778·67	[... 77·83]	·03

The values of F(1.2), F(1.3), corrected as explained in the text, are :—

(107)	(102)	(107)	(102)
80151.87	...157.23 ⁽¹⁾ *	103500.09	103505.45
269.55	...274.91	...607.71	...607.71
334.67	...340.03 ⁽¹⁾ *	105528.21	105533.57
451.71	...457.07 ⁽¹⁾ *		
82180.0	...185.55		

⁽¹⁾ These are sustained by $3h\nu$, $2h\nu$ affects :—

$3 \times 26719.0 = 80157$	1n 3741.7	$d\lambda = +0$
$2 \times 40171.44 = 80342.88$	1 ii 2488.58 D.	„ = -0.09
$4 \times 20114.50 = 80458.0$	1, 4970.30 W.	„ = -0.06

F(1.*m*). 2. 1247.6; ...45.7; ...44.7; ...43.0; ...16.8.—3. 966.2; ...65.2; ...47.6.

F(2.*m*). 3. 3790.4; ...75.697; 24.000; ...05.368.—4. 2705.358; ...02.470; 2668.77 D.; ...66.30 D.—5. (2341.54; ...39.37; ...14.39) D.—6. (2168; ...66.24; ...44.67) D.—7. 2070.60 D.—8. 2008.55 D.

F(3.*m*). 5. 5707.7 Bl.; 5637.710.—6. 4781.0 Stk.; ...29.9.—7. 4327.025; ...04.0.

Notes.

$m=3$. The line 26375 is given by both W. and Bl. as an arc line. E.V., however, give it as a spark line of intensity 8, and Steinhausen definitely states it is enhanced. The F_{22} is not observed, but the value entered in [] is derived from 26845.239 as $F_{22}(-6\delta_1)$. There is evidence of considerable disturbance in this region. In succeeding orders there seems to be disruption into a normal set (Class E_1 and displaced from the calculated values), and another shifted about 39. In the table these are placed in (—). The formula is calculated from 26375 and 36992 as $F_{12}(2.m)$ for $m=3, 4$. The calculated values for $m=5, 6, 7, 8$ are 42685.09, 46087.77, 48281.53, 49777.83.

$m=4$. As they stand in the table, the four lines appear at first sight to form an excellent F type, with the last as a forbidden F_{31} . The apparent satellite separation of 39.51, however, does not satisfy the own multiple rule— $14\delta_1$, $15\delta_1$ require 38.05, 40.76—and especially it occurs in succeeding orders. They must, if admitted as F, therefore be due to a parallel series with displaced $d2$. Here $3\delta_1$ on d_12 shifts 42.73. F_{12} calculated from the formula based on F(1.2), F(1.3) is 36983 so close as to support 36992. There would seem to be no satellite.

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$m=7, 8$. The ff combinations seem to support the calculated values, as do also the $F(3.m)$ distinctly.

$m=5$. The direct 224·6 in $F(3.m)$ does not appear. But it appears back to 1 iii, 17290·809. This, if not a coincidence, must be a linkage effect; in other words, a case where an electron falls from f_5 to d_13 and another raised from d_23 to d_13 either simultaneously or before the emission takes place.

ff Combinations.

f_22-f_23	23348·221	3 ii 4282·781
$b f_12-f_23$	23164·650	1 4315·713
$a_1f_22-(102)f_13$	23332·8	3 ii 4284·6 P.
$a_2f_22-(107)f_13$	23325·56	1 4285·942
cf_12-f_13	23151·3	1 4818·3
$a_1f_22-f_4$	33851·7	1n 2953·3
$a_1f_22-f_5$	39552·90	1 iii 2527·50 D.
$a_2f_22-f_6$	42938·99	1 ii 2328·17 D.
f_12-f_7	45075·04	0 ii 2217·83 D.
f_12-f_8	46574·92	1 ii 2146·40

TABLE VIII.—G.

$bf_12=52120·09$. $cf_12=52003·05$. $f_13=28852·59$.
 $bf_1- = 13·024$; $f_2- = 13·093$; $cf_1- = 12·980$; $f_1- = 5·365$;
 $f_2- = 5·395$.

$$g_2m = 4R/\{m + \cdot 933582 + \cdot 102144/m\}^2.$$

$$G2.m. \left\{ \begin{array}{l} b \ 23267·50 \\ c \ 23150·46 \end{array} \right\} G3.m.$$

5·092.				
3.	1	24147·635		
	2	330·580	182·94	
2·608.				
4.	1	34290·6	(23267·6)] L
		(173·55)	(23150·5)	
	$G_{11}?$	[188·5]	15 (23150)	1 [11023·0]
	1 i	360·1	186±	11038±1
	G_{21}	1 iii 484±6	296±	[11125·2] 15 (102·2)
1·519.				
5.	2 i	39619·36	(23150·46)	[16468·90]
		(802·64)	183·28	1 i 16573±2 104±2

TABLE VIII.—G. (*cont.*).

·947.						
6.	1 ii	42938·99	(23149·2)	1 i	19789·8	
	1 i	55·04	16·05	2 i	803·1	13·3
	— — —			0	893·737	102·9
·633.						
7.				2	21907·99	
				2 iii ?	913·1	5·1 $8\delta_1$
				1	22012·5	104·5
·444.						
8.				1 i	23371·211	
				2	473·7	102·5
·323.						
9.				2	24425·1	
				1	527·776	102·7
10.				1 n	35196·0	
				1	303·515	107·5

G(2.*m*). 3. 4140·182 W.; ...08·899.—4. 2915·5; ...25·385; ...09·5 Bl. 2899 Bl.—5. 2523·26 D.; ...11·64 D.—6. 2328·17 D; ...27·30 D.

G(3.*m*). 4. 9057 McL.—5. 6032 Bl.—6. 5051·8; ...48·4; 25·563.—7. 4563·27 P.; ...62·3; ...41·7.—8. 4277·569; ...59·0.—9. 4093·1; ...75·864.—10. 3967·9; 3950·906.

Notes.

$m=3$. The observed should be somewhat larger than the extrapolated value of 24134. The line given satisfies this, but it is one of a complicated set of collaterals.

$m=4$. The calculated $G_{12}(2.4)$ are $cG=34163\cdot9$, $bG=34281\cdot6$. These should be the observed 34290 and a line covered by the neutral S_1^{34} , 34173. The $G(3.4)$ are in a little observed region, and the $G_{11}(2.4)$ in the list is very doubtful. Taking it as corresponding to $G_{11}(3.4)$, it gives a forbidden G_{22} of class iii.

$m=5$. (16477·07; 16579·31) for $G(3.5)$. The second settles the observed G_2 , and the unobserved G_{12} gives the exactly observed $G(2.5)$; but $G_2(2.5)$ is covered by the neutral $D_{11}^3(17)$.

$m=6$. [19771·53.] The obs. are 18·3 ahead of the calculated, which is excessive for an order one less than that of the formulæ standards. Again they are in a complicated complex of related lines (see below).

$m=7, 8$.—These are taken as standards for the formula.

Raw Material for G(3, 6, 7, 8).

6.			7.			8.		
4 i	19747·6	(6·94)	1n	21837·0	(7·91)	2 iii	23291·49	(3·88)
3 i	849·1	101·5	2n i	940·0	103·0	1n	394·72	103·23
1 i	19789·8	(6·957) A	2	21907·99	(7·95) A	1	23325·55	(8·91)
0	892·74	102·9	1	22012·5	104·5	3n	428·05	102·50
1n	19808·6	(9·966)	1 iii	21988·547	(7·995)	1 i	23371·211	(8·94) A
2 ii	911·6	103·0	1	22093·3	104·8	2	473·7	102·5
2 ii	12921·5	(7·01)				3 ii	23441·970	(9·05)
1 ii	20025·95	104·4				1	545·0	103·0

A denotes the lines taken as representatives of G. The figures in () give the denominators of *gm*.

m=6. In this column not only does 19789 show a *cf* separation to G(3.6), but we also find

1n	19808·6	(23269·1)	1 i	43077·74	
2 ii	19911·6		5	43194·63	117

This gives the *bf* separation within $dn=1·6$ or $d\lambda=.4$ on E. V.'s excessive measure, and perhaps the difference 23269 is a near coincidence. The set would fit, however, in the G(6) scheme as G_{11} , with a satellite separation of 18·8 ($20\delta_1=18·94$), in which case 19911 would be a forbidden G_{21} , and the class ii would be explained. The corresponding G_{12} and G_{22} in the G(2.6) or 43059, 43241 have not been observed. The set would appear to fit in better in the following schemes, in which case 43077 is not a G(2.6) line. The two observed 19808 and 19789 are separated 38, 19 from the calculated $G_{12}6$. The values of f_13- and g_2- being respectively 5·365, ·947, ($-3\delta_1/(3\delta_1)$) shifts 18·9. In fact, if the calculated value be taken as G_{16} , the whole set in this column may be represented in a collateral scheme as given below, in which the first column gives the collateral notation, the second the calculated W. N., and the last the observed with O—C $d\lambda$ values. In forming this it must be remembered that an own displacement in the limits f_1, f_2 alters the doublet separation by ·03. The calculated $G_{12}6=19771·53$ requires correction for formula error, and this is obtained from the very accurate observed 19892·737. The

separation 102.35 corrects 19789.8 to ... 90.39. This as $(-3\delta_1)G(3\delta_1)$ gives G as 19771.46 or $O-C\,dn = -.09$, $d\lambda = .02$.

$(5\delta_1)/(-3\delta_1)$	19747.48		4 i 19747.6		-.02
	849.59	102.11	3 i 19849.1	101.5	.1
$G_{1.6}$	$\left[\begin{array}{c} 19771.46 \\ 873.72 \end{array} \right]$			102.26	
$(-3\delta_1)/(3\delta_1)$	19790.39		1 i 19789.8		.1
	892.74	102.35	0 892.737	102.9	0
$(-6\delta_1)/(6\delta_1)$	19809.32		1 n 19808.6		.1
	911.76	102.44	2 ii 19911.6	103.0	-.02
$(-2\delta)(G_2(6\delta_1))$	19922.74		2 ii 19921.5		.2
$=(-27\delta_1)G_1(6\delta_1) $	20025.73	102.99	1 ii 20025.952	104.4	-.1

The last line is directly calculated, and differs from the second of the reliable measures by $dn = .22$. This involves the O.E. of the other as well, say .10 or $d\lambda = .02$ on each. It is noticeable how the displacements on the g term are all multiples of $3\delta_1$, and on the f with the exception of the first.

$m=7$. In this set are observed two apparent bf , $G(2m)$ — $G(3m)$ separations 23267.50, viz. :—

21837.0	23268.9	1 i 45105.95
21988.54	...65.43	0 i 45253.97

The first is the bf separation within O.E., but the measures in the second do not admit this, at least directly. In the first it means that 21837 must contain the term bf_13 unaltered. Then the W.N. differs from 21908 ($G7$), too much to be explained on a satellite basis. If, then, the bf relation is real, the two lines must be related on a linkage basis. Their separation 71 suggests the difference of two p -links. In that case we should expect to find the singly-linked line. We find such at 31167.0, with a parallel inequality due to a $6\delta_1$ displacement due to β and the $(70\frac{1}{2}\delta)$ link 9262.80. The scheme is given thus, with l standing for this link and additional linked line.

G	21907.99				
	9262.80	G. l			$G(-6\delta_1). l$
		(31170.79)	3.79	$(6\delta_1 \equiv 3.80). 1, \dots 67.0$	
	9333.79		9120.45		
$\beta. G. l$	21837.0	$d\lambda = .08$	2 i 40291.24		$G(-2\delta_1). \alpha. l$

$m=8$. The only *bf* relation is a very exact one on the first :—

$$23291\cdot491 \quad 23267\cdot38 \quad 0\text{ iii } 46558\cdot87$$

both class iii lines, which excludes the set from being a normal G. Its close *bf* ($d\lambda=0\cdot04$) settles that it belongs to the system without any displacement on the $f_1 3$ limit. This whole region is a very puzzling one, being crowded with lines related by chains of 183, 300 separations, showing, therefore, the presence of $f(2)$ terms, unless these $f(2)$ separations also act as links, a supposition not to be pedantically set aside.

TABLE IX.

The $nh\nu$ sets.

In S_2 &c. lines the values corrected for the exact ν separation are placed in (). The d_n corrections in observed to meet these are placed after the wave number, and the last column gives the O—C $d\lambda$ on these observed lines.

$S_1 1$	57495·30	3 (19165·044 + ·05)	1 i 5216·384	·01
		2 (28745·11 + 2·5)	1 3478·00 W.	·3
$S_2 1$	47772·65 (·22)	2 (23885·238 + ·87)	1 4185·511	·14
$S_1 2$	35104·16	2 (17552·5 — ·4)	1 5695·7	—·1
$S_2 2$	44190·755	2 (22093·3 + 2·05)	1 4525·1	·4?
$S_1 3$	61578·06	2 (30789·7 + ·7)	3 iii 3246·9 Bl.	—·08
$S_1 4$	73030·73	3 (24343·341 + ·23)	2 4106·745	·04
		2 (36525 — ·9)	1 ii 2737 Bl.	—·7
$S_2 4$	82877·5 (60·40)	2 (41438·2 + ·55)	0 ii 2412·5 D.	·03
$S_2 5$	88550·4 (47·0)	4 (22136·3 + ·4)	4 4576·4	·08
		3 (29516·289 — ·6)	3 i 3386·991	—·07
		2 (44273 + ·5)	0 2258 D.	·02
$S_2 5$	88865·2 (6·3)	4 (22217·5 ⁽¹⁾ — ·9)	1 iii 4499·8	—·2
$S_1 6$	82580·94	3 (27528·2 — 1·2)	1 3631·7 Stk.	—·1
$S_1 8$	86385·98	2 (43194·62 — 1·63)	5 i 2314·39 D.	—·09
$S_2 8$	96237 (51·3)	4 (24060·6 + 2·2)	1 n 4155·1	·4
$S_1 9$	87477·28	4 (21869·0 + ·32)	1 iii 4571·5	·06
		2 (43739·03 ⁽¹⁾ — ·39)	0 2285·58 D.	—·02
$S_2 9$	96646·4 (32·4)	2 (48316·10 + ·1)	0 ii 2069·04 D.	0
$S_2 11$	98212·5 (8·3)	3 (32737·7 + 1·7)	1 iii 3053·7 Bl.	·17
$S_2(3\cdot4)$	26828·81	2 (13414 + ·4)	2 7453 W.	·2
$S_2(3\cdot5)$	32772·23	2 (16386 + 0)	2 i 6101 Bl.	0
		2 (16416 — 3·0)	2 i 6090 Bl.	1

TABLE IX. (*cont.*).

$S_1(3.6)$	33360 (59.3)	2 (16678 +1.6)	1 i	5994 Bl.	.5
$e, S_2 3$	[50620.72]	2 (25310.274 + .08)	1	3949.851	.01
$e, S_1 5$	58424.60	2 (29210.9 +1.4)	1	3422.5 Stk.	.1
$P_1(1.3)$	106716	3 (35577 -5)	1 ii	2810 Bl.	.4
$P_2(1.3)$	103928 (31.1)	2 (51962.17 +2.4)	0 iii	1923.81	.08
$P_1(1.4)$	124768	5 (24953.846 - .24)	3 ii	4006.270	-.04
$P_2(2.5)$	40096.52	2 (20048.2 + .05)	3	4986.7	.01
§	40784.65 . β	2 (25059.006 + .02)	2	3989.457	0
§	50617.53	2 (25308.9 - .13)	3	3950.2	-.04
§	51321.79	2 (25660.733 + .16)	1	3895.254	.02
$P_2(2.6)$	45230.83	2 (22615.5 - .08)	2 iii	4420.6	-.01
$P_1(2.7)$	48482.91	2 (24241.07 ⁽²⁾ + .38)	1	4124.071 Cd.	.06
$p2, p3$	55674.9	2 (27837.507 - .03)	2 n	3591.255	0
$D_2(3.5)$	32527.8	2 (16263.79 + .11)	3	6146.93 P.	.03
$D_{11}(2.6)$	82573.22	2 (41286.73 ⁽³⁾ - .11)	0	2421.35	.00
$d1 d2$	76634.2	2 (38317 + .1)	0	2609 D.	0
†	77106.9	2 (38555.19 -1.7)	1 iii	2592.91 D.	-.1
†	77154.5	3 (25718.999 - .13)	1	3887.079	-.02
†	78559.48	3 (26187.199 - .70)	1	3817.571	-.15 ??
		2 (39279.4 + .35)	1 ii	2545.1 D.	.02
$d1 d3$	102084.3	2 (51040.98 +1.17)	0 i	1958.57 D.	-.04
†	104385	3 (34793.693 +1.3)	1	2873.243	.1
$F_{12}(1.2)$	80157.23	3 (26719.0 + .03)	1 n	3741.7	.00
$b, F(1.2)$	80340.03	2 (40171.44 -1.33)	1 ii	2488.58 D.	-.08
$eF(1.2)$	80457.07	4 (20114.50 - .24)	1	4970.50 W.	-.06

 $2/\nu$ lines to unobserved series lines.

$S_2 1$	2 (24098.9 - .25)	48197.30	9298.09	$70\frac{3}{4}$	1	4148.6	-.04
$S_2 2$	2 (22164.8 +1.03)	44331.67	9227.51	$70\frac{1}{4}$	1	4510.5 Stk.	.2
	2 (22182.964 + .52)	44336.96	9262.80	$70\frac{1}{2}$	2 iii	4507.704	.1
	2 (22217.5 ⁽⁴⁾ +1.3)	44437.6	9333.41	β	1 iii	4499.8	.25
$S_2 3$	2 (35669.186 - .85)	71336.67	9758.61	74	3	2802.716 Cd.	-.06
$S_2 4$	2 (41074.37 +1.9)	82152.53	9121.80	α	2 ii	2433.87 D.	.1
	2 (41233.78 +1.31)	82470.18	9439.45	$71\frac{3}{4}$	1 iii	2424.46 D.	.08
	2 (41286.73 ⁽³⁾ +1.46)	82576.38	9545.65	$72\frac{1}{2}$	0	2421.35 D.	.08
	2 (41358.29 + .85)	82718.29	9687.56	$73\frac{1}{2}$	1	2417.16 D.	.05
$S_2 8$	2 (47755.07 -1.18)	95507.88	9121.80	α	0 ii	2093.35 D.	-.05
$e, S_2 4$	2 (31124.47 - .30)	62248.34	9829.67	γ	2 iii	3211.98	-.03

§ Of linked. See notes to P(2.5).

† Of collaterals. See notes to the dd table.

TABLE IX. (*cont.*).

$e. S_2 8$	2 (37428.9 +1.35)	74860.57	9086.59	69 $\frac{1}{4}$	3 i	2670.94 D.	.1
$P_2(1.3)$	2 (51940.0 -1.14)	103877.72	2838.28	69 $\frac{3}{4}$	0 iii	1924.7 D.	-.04
$D_2 4$	2 (41212.52 ⁽⁵⁾ + .9)	82426.85	9439.45	71 $\frac{3}{4}$	2 ii	2425.61 D.	.05
	2 (41373.86 - .85)	82746.01	9758.61	74	1 i	2416.25 D.	-.05

(¹) This is S_2^{310} with $d\lambda = -.12$, larger than here, but S_2^{310} is definitely here. The $\frac{1}{2}S_1 9$ possibly occurs especially as $\frac{1}{4}S_1 9$ does, but it is overlaid by this definitely arc line.

(²) Observed by S., but not by Bl., and so is not classified, but Cd. gives it as seen in the arc, and not in the spark.

(³) This is also $\frac{1}{2}S_2(2.4)$ for an observed S_2 , and also is a $S_2(3.9)$, but the latter's separation value (74 $\frac{1}{4}$ δ) is exceptional. The $\frac{1}{4}D_{11}$ must be accepted at least.

(⁴) $\frac{1}{4}S_2(5)$ with γ and $\frac{1}{2}$ unobs., $S_2 2$ with β . The observed line is actually the mean of these two, and may be a merge.

(⁵) Is also a $S_2(3.9)$.

Perhaps the most remarkable fact emerging is that while a small proportion of the numerous S_2 lines occur, all the S_1 examples from $m=1$ to 9, with the only exceptions of $m=5, 7$, are seen, even in the cases where S_1 themselves are wanting. This systematic effect points to the relations as being real, and not mere coincidences.

It is clear from the nature of the emission that no $n\hbar\nu$ line can show a link connexion, unless the original line is connected with an n -fold chain of the same link. For this reason I have tested each of the lines in the above list. My hand-list of wave numbers is a maze showing link connexions from the vast majority of the lines. Yet it is remarkable how all the above, with few exceptions, show none. This seems a clear indication that they are of a special nature. I do not discuss the exceptions here, but there are two which are specially important as having been used as evidence for establishment of relations in the mercury spectrum. They are two, viz., the $3\hbar\nu$ for $S_1 1$ and $F_{12}(1.2)$. In the former 19165 shows a possible back α link to 10044. This is explained by the fact that 10044 is itself also a $3\hbar\nu$ for the emission $\hbar\nu=30133.45$. Thus

$$\begin{array}{rcccl}
 S_1 1 & 9123.34 & S_2 1 & 9125.71 & 39246.25 & \mathbf{9112.80} & 30133.45 = 3 \times 10044.46 \\
 & \alpha + 3\gamma + .18 & & & \alpha + 9\gamma - .18 & & \alpha - 20\gamma + .09 \\
 & & & & \text{obs.: } \dots 44 & 2, 9953 &
 \end{array}$$

The total separation is $3\alpha - 8\gamma + .09 = 3$ (9120.68).

In $F(1.2)$, 26719.0 shows a back γ link = 9289.0 to 16890, 1 i 5919 Bl. Here again 16890 appears as a $3\hbar\nu$ to an observed line. Thus

$$3 \text{ iii } 1972.72 \quad 50674.74 = 3 \text{ (16890 + 1.58)} \quad d\lambda = .3 \text{ on } 5919$$

PART II.

Relation to Allocations by Paschen.

The line $n=35104$ has been taken, both in Part I. and by Paschen, as S_12 in the two systems of allocations. In other words,

$$35104 = 92034 - s2 = 90661 - as2,$$

where, to avoid confusion, *as* stands for Paschen's *s*-term. These cannot both subsist. Either there must be some error in one of the $p2$ limits, or the line cannot belong to both systems. The 92034 is quite definite if the assumptions which form the basis of Part I. are sustained. They stand or fall together. The 90661 depends on the connexion between series $p2-tm$ and $p3-tm$, in which the second is sufficiently numerous to give the value $p3$, and only an allocation for one common order m gives a relation between $p2$ and $p3$. Either, then, this relation must be defective, and give an erroneous value of p_12 , or the line cannot belong to both series. This is the question which it is proposed to discuss in this Part II. Paschen's P and S allocations are collected together into two tables given at the end.

1. Taking the three lines for $m=3, 4, 5$, in Paschen's $P_1^2(2.m)$ sets, we get the formula

$$n = 55925.33 - 4R / \{m + .180792 + .434404/m\}^2$$

The limit ($s2$) is 360 larger than that given by Paschen, but the possible error in its value must be much less than this, if the set forms a real series. With this limit and the $P_1(2.3)=16257$ there results $p_13=39668$. The $S(3.m)$ series gives, using $m=4, 5, 6$ a limit $p_13=39297.76$, which practically agrees with Paschen's value. These two values for p_13 differ too much to be ascribable to formulæ errors, and seem to point to some error in allocation of at least one of the two sets or to the presence of collaterals.

With $s2=55925$ the p_12 term determined from $S_1(2.2)=35106$ is $91031.47 + \xi$. To produce a separation of $9121.88 + d\nu$ in this requires a displacement of

$$102335 + 10.498d\nu - 1.609\xi = 70\frac{1}{2}\delta + 104 + 10d\nu - 1.68\xi.$$

No possible values of $d\nu$ or ξ can make this satisfy the own law; nor can the succeeding p_13, \dots be met by own

multiples without excessive and arbitrary changes in the limit. If, however, the value of $p_1 3$ be taken from the above $S(3, \infty) = 39297.76$, the $p_1 2$ deduced in a similar way is 90661, and this exactly obeys the own law. The displacement is

$$102957 + 10.507 \, dv - 1.625 \, \xi \\ = 71\{1450.099 + .148 \, dv - .013 \, \xi\} = 71\delta.$$

But again none of the higher order separations can be met. Expressing them in terms of order of magnitude, *i. e.*, of nearest own multiple, we find, with the limit $s_2 = 55925$,

9122	3673 (3424)*	853	262	199
70½δ	99¼δ (93δ)	57½δ	41δ	37½δ

* See below.

The 99¼ (100¾ on the 90661 limit) is a far larger multiple than in any known case. These multiples show in some cases a steady rise with increasing order, or more generally a steady fall from the first one, but I know of no example in which there is a rise followed by a fall. The rapid fall here, however, is analogous to those in Zn ii and Cd ii as allocated by von Salis.

The λ/m term in the formula is positive, contrary to the usual rule for p terms, and, moreover, is very large. Indeed it is small and negative in the Zn ii, Cd ii. We should hardly expect, then, to get very accurate extrapolation for $m=2$, and only roughly near ones for $m=6, 7, 8$. The extrapolated values for these latter are 44706.42, 47562.69, 49456.21. These suggest the sets added to the P list of 44709, 47584, 49466, which agree within formula errors with the corresponding $P_1(3.m)$ observed lines as allocated by Paschen (see the table, wherein additional lines are added, denoted by †. In extrapolation to lower orders changes in the mantissa indicated by a formula seem to be exaggerated in the observed. Here we then expect for $m=2$ a denominator somewhat greater, or a term p_2 somewhat less than the extrapolated value, here [76292.86], which gives a negative value for $P(2.2)$, *i. e.*, it gives $p_1 2 - s_2 = 20367.53$. We find near this two pairs:

2 i 4913.0	20348.9 [7.43]	(43.16)	1 i 4902.853	20390.609
	9120.3			9121.99
4 ii 3392.397	29469.252		1 3387.414	29512.602

These sets, both giving the proper 9121 separations, are clearly related to the $P(2.2)$ of this series—either as both

collaterals of the normal P(2.2) or one as P(2.2) and the other a collateral. We note

- (1) Any displacement can only occur on the s_2 term, otherwise the doublet separations would be largely altered. If the 20348 be corrected from the good measure $29469.252 - 9121.80 = 20347.45$, the separation from the second is 43.16. The $s_2 = 14.476$, so that $3\delta_1$ shifts 43.43, and explains their relative displacement.
- (2) The extrapolated $p_{12} = 76292.86$ is in better step with those for Zn and Cd. Thus

$$\text{Zn } 97892, \text{ Cd } 89750, \text{ Eu ?}, \text{ Hg } 76292.$$

- (3) The displacement on $76292 + \xi$ to produce 9120.80 is $90\frac{1}{2}\delta + 60 - 2.45\xi$. A value of $\xi = 25$ on a formula extrapolation is not excessive, so that the value of $p_2 = 76317$ is in step with the other elements, and obeys the own law, although with a very excessive multiple.

2. The $-P_1(2.2)$ or S_{12} then belonging to this series cannot be 35104. It would appear that the formula, in spite of its abnormal form, fits a regular series of some nature. The positive value of α/m suggests that, if a real series, it refers to a d, d . Also the limit may be written as $4R/\{2.800829\}^2$, with a mantissa 8×100104 , again suggesting a d_2 term analogous to those discussed in Part I. Indeed, it is possible to make additions to the set as given by Paschen to give it the appearance of a dd series with a d_2 separation of $3423 \pm$; or we may arrange new lines in which this separation replaces 3673. The first case is illustrated by additional lines in the P list in (). On this supposition 62δ in the limit produces a separation 3424.6. The second is illustrated by additional lines, also in (), in the S list. On this supposition a displacement of 93δ is required to produce 3423.74 in the p_3 term. The march of the new separations is now superior to that of 3673, but still remains anomalous. We may add that 3673 occurs also in connexion with $P_1(1.2)$ or 60607, and quite out of place. The corresponding line is due to Ly., and to determine a satisfactory measure we use both of his measures. They are

$$9, 60615 \quad 3667 \quad 2, 56948 \quad .$$

But both arrangements seem to be rather examples of the danger of trusting equal separations as necessarily referring to bi-term lines, especially in very rich spectra where numerous links occur. I believe I have shown*, for instance, that such trust vitiates the arrangement of terms in the spectrum of copper as given by both Shenstone and Sommer. In the present case it may be noted, in illustration, that $3673 - 3424 = 249 = 7 \times 35.7$, which suggests that the two values differ by the difference of two p_2 terms (or links) due to $m\delta_1$ and $(m+7)\delta_1$. Also the neutral c link is 5481.07 and 9157.03 ($69\frac{3}{4}\delta$)— $c = 3675.97$.

3. We may further criticise the "P(2. m)" lines from another quarter. They are all closely associated with the α , β , γ separations, but whether as links or as themselves containing p_1^2 terms is not at once evident. The latter would definitely exclude the set as being a P(2. m) series. If we complete the α , β , γ maps, we find the lines associated with near lines showing the satelloidal effect. We have learnt in the case of copper that such lines include the p term, and possibly only the lowest p term. Again, then, we have a doubt suggested that the series in question is not a P(2. m). It will be sufficient to illustrate this by giving the results for one only, viz., the "P(2.3)," in which the P_1 —16257—has itself a near line separated from it by 6.79 with $15y = 6.805$. The lines adduced are all successive.

		3 ii	25356.863		
		2	59.138	2.27	$5y + 0$
		1	70.98 P.	11.84	$26y - .04$
9120.03		1	77.032	6.05	$13y + .15$
($\alpha - 4y + .04$)		8b	80.39 Cd.	3.36	not M(y)
16257.00					
263.79	6.79	4A	25591.284 ⁽¹⁾		
9334.80		4n	.800 Cd.	.516	$y + .06$
($\beta + 3y + .03$)					
		1	26072.948		
		1	78.4 E. V.		2×2.72
9828.53		1 iii	85.534	12.586	$16y = 7.22$
($\gamma - 3y + .18$)					$28y - .11$

(¹) This is neutral D1(4). Here it must be chance coincidence.

* See specially Phil. Mag. 4, 1207-9, 1929.

		3	21687.24 P.		
	9118.30	2	701.92 P.	14.68	$32y=14.518$
	$(\alpha-8y+.13)$	1 i	13.671	11.75	$26y=11.795$
		2	21907.99 P.		
12583.62	9329.36 ⁽¹⁾	2n iii ?	13.1 E. V.	5.1	$11y=4.99$
	$(\beta-9y+.03)$				
		3 i	22394.7 E. V.		
		1	408.2	3.5	$7y=3.18$
	9835.73	1 iii	19.354	11.1 14.6	$32y=14.52$
	$(\gamma+13y+.12)$				

(¹) If the line is corrected by $11y+0$ to 21912.98.

It will be seen that these near lines show separations all very close multiples of the sateloid constant y . Whether individual examples are real cases or not the general consensus of the whole is in striking support of the existence of this effect in connexion with the lines linked to these P(2.3). The appearance of these α , β , γ may of course be due to a concurrence of three links on the same line, but the most natural conclusion to draw is that they occur because the original lines 16257 contain the $p_1 2$ term, and the others the respective $p_2 2$ corresponding to α , β , γ . If so, we should further expect to find lines corresponding to other p_2 lines. An inspection gives the results for 16257.00, ... 63.79 indicated in the following list, in which the first two columns give all the successive δ multiples and the corresponding true separations. The details for 12583 are omitted, but the existence of the effect here is indicated by attaching a † to the value in the second column. A * indicates that the same separation occurs in the S(2. m) allocation of Part I.

The corrections to be applied to the observed separations to make them equal to the standard v in the second column are indicated on the left of the observed W.N. The figures in thick type on the right are for use later.

The greatest deviation entered is that for $69\frac{1}{4}\delta$, but is accepted, as the observed difference 2.74 is the persistent sateloid 2.72 effect. The others are met by small y -multiples with great exactness, as indicated on the lists. That for β or 71δ must be excluded, since it is an arc line (Bl.), and, indeed, is D¹⁴—or, if it is covered by this, it affords no evidence for our purpose. But including it,

a first glance shows a tendency for the representatives to appear in sets of three successive ν with that for 748 absent. For this, however, a line 2, 26012.313, giving 9755.31, with defect 3.30, might possibly be accepted, since $7y=3.176$. This table seems to give decisive evidence that these lines contain the p_1^2 term, and further, that as the separations are all forward, p_1^2 must enter as a positive term. In that case, if a bi-term line, *i. e.*, as $p_1^2 - t$, the t -term in 16257 would be

$$92024.34 - 16257.00 = 75767.34 = 4R / \{2.406300\}^2,$$

quite out of step with known terms in other elements of this group. If it is linked with S_1^2 or 35104.16, the linkage value must be -18847.16 . The same link attached to my allocation of $S_1^3=61580.1$ should show a line at 42733.0, and this is found at 4 i, 42733.362. The same linkage also is found with the extrapolated value for $m=2$ in the suggested completion of Paschen's " $P(2m)$," viz.,

3423.12	23771.452	18849.40	On ii	42620.85
	29469.25	18846.95	4 i	48316.10
	20348.33			

These repetitions give support for the reality of the linkage origin of 18847. The value is closely met by the sum of two p_2 links—thus $9051.41 + 9794.17 = 18845.58$. The lines given in the above list would represent the intermediate one-linked lines. The separations from 35104 are given by the figures in thick type on the right (9 omitted). It must be noted, however, that on this basis only one pair can serve to unite 35104 and 16257, and the other separations shown in the list can be attached to one of the two lines only. This double linkage is clearly seen to be near that entered in italics, the links being for it, and the two next:

$$\begin{aligned} 9086.59 - 6y - .02 + 9758.61 + 10y + .06 \\ &= (69\frac{1}{4}) + (74) + 4y + .04, \\ 9120.03 + 9727.13 = \alpha - 4y + .04 + (73\frac{3}{4}\delta) + 9y - .03 \\ &= \alpha + (73\frac{3}{4}) + 5y + .01, \\ 9192.26 + y + .04 + 9652.06 + 5y + .08 \\ &= (70) + (73\frac{1}{4}) + 6y + .12. \end{aligned}$$

From the nature of the case, near values of ν must give closely similar results, so that it is not possible to definitely settle which gives the true double linkage. We shall provisionally accept the second of these, not only because it shows the smallest error ($\cdot 01$), but because it involves the two separations α and $(73\frac{3}{4}\delta)$ which occur in §3 of Part I as of most frequent occurrence. A consideration of the other separations shows that nearly all the other cases are linked to 16257, and not 35104, but it is here omitted as of little interest for the present purpose. We seem, then, driven to the conclusion that the proposed $P(2.m)$ lines are really of the form $p_1 2 - tm$, with linkage effects added.

4. Passing now to the proposed $P(1.m)$ sets, 111969 is given as $P_1(1.3)$. It is separated 95712 from 16257 or " $P(2.3)$." If these allocations be accepted, this is the value of $s_1 - s_2$, which again is sustained by the fact that the $S_2 - S_1 = s_1 - s_2$ has the same value, and there is no doubt but that $S(2)$ is at least one real $S_1 2$ line of Hg. If however, the doubt as to 16257 being $P(2.3)$ is justified, it would follow that the allied 111968 set do not belong to $P(1.3)$, and that $s_1 - s_2$ is not 95712. It would then follow that 60607 is also not $P(1.2)$. But the double appearance of 95712 as

$$S(2.2) + 60607 \cdot 6 = 95713 \cdot 7$$

$$\text{and} \quad 111968 \cdot 6 - 16257 \cdot 00 = 95711 \cdot 6$$

can scarcely be a coincidence, but must indicate a relation with the S_2 lines, either some change from a s_2 term to some other, or this combined with a linkage. It may be significant that $95711 \cdot 6 - 92034 \cdot 6 = 3677 \cdot 0$ close to Paschen's 3673.3. Also 60609 seems to show the same 3673 separation as the $P(1.3)$ (see above). To these considerations may be added the following.

- (1) The example I in the link discussion of §9 shows that the 60609 has a very exact series inequality with D_{23}^{35} .
- (2) Although the intensities of 60607, 51484 are large, they make P_1 much less intense than P_2 instead of twice as great, the normal value. This large discrepancy can scarcely be due to extra absorption of the P_1 by the vapour. It must however

be confessed that the observed absorption of 51484 by ionized vapour supports its allocation as depending on one of the lowest levels. On the other hand, the statement by Williams referred to in § 2, that it is a "raie ultime" would definitely relate it to the neutral atom.

- (3) If Paschen's relations of the S. P lines be accepted, $s_1=151268$, $p_1^2=90661\cdot9$, and the denominators of the lines are as follows :—

	$p.$		$s.$
60707	2·201003	—60707	1·702068
111968	3·341145	35106	2·810129
p_{14}	4·322842	60807	3·833442

The change in mantissa between the lower two levels in both seems excessive, and in 2·201003 is in the *wrong direction*. Accepting 60707 as P1 of this system, the latter abnormality seems to me fatal against 90661 being p_1^2 , *i.e.*, against 35106, from which it is deduced, as being S2 of the same system. Also the *sm* formula determined from $m=4, 5, 6$ is of quite normal form and has a small α/m term, so that the calculated s_2 should only have a small error. The formula gives $s_2=55077\cdot73$, with resulting $-S(3,2)=P(2,3)=15780$, instead of 16257, and not sustaining 90661 as p_1^2 , or accepting 90661 as p_1^2 , it gives $S_2=35583$. The latter as an extrapolated value to $m=2$ agrees very satisfactorily with the observed very strong line 10, 35514·43, only observed by Paschen. He has taken this to be $s_1-d_1^+$ where d_1^+ is a *d* term analogous to that of the well-known $\lambda=5105=p_1-d^+$ in the spectrum of copper. But it, as Paschen himself has pointed out, is forbidden on two counts, as being a transition from *d* to *s* and from $j=3$ to $j=1$. Forbidden lines have a way of existing in spite of legislation laid down for them, but it is hard to accept that they can be of such high intensity as Paschen has found for them. Also he has allocated 25093·6 to an analogue of the Cu line $\lambda=5105$ as $d_1^+-p_1^2$. But in Cu this line is a single line of great sharpness, whereas, as we have seen in the No. 20 in the satelloid list of Part I. Cardaun has given it complex with four companions, and Runge and Paschen in 1902 gave it as triple. The Zeeman pattern is diffuse, probably

owing to the superposition of the companions. Paschen seems to accept the allocation of this 5105 as a $-D_{11}^+$ to the 5782, 5700 as $-D_{22}^+, -D_{12}^+$. But the characters of the two sets are completely different, and I have attempted* to show that this supposition cannot be sustained.

5. Paschen has noted a relation between three lines to which he has given the allocations shown herewith:—

$$60607.6 - 25093.6 = 35514$$

$$s1 - p_1 2 - (d_1^+ - p_1 2) = s1 - d_1^+$$

If, however, 35514, as suggested above, is the S2 of his system (say) $ap_1 2 - as2$, 25093 must be $as2 - t$ and 60607 $ap_1 2 - t$. The extrapolated $as2 = 55077 + dn$ would then give

$$t = 29984 + dn = 4R / \{3.825130 - 63.8 dn\}^2.$$

To compare with this denominator we have those of Paschen's $d3 = 3.839$ and the $s3, d3$ of Part I., viz., 3.7961, 3.8161. In analogy with the 26473 as $s2 - s3$ of Part I., it would seem natural to give to it the similar allocation here of $as2 - as3$ and to 60607 that of $ap2 - as3$.

6. The foregoing discussion is a criticism of that part only of Paschen's allocations which involve the lowest p_1 term. Indeed a part of it is based on the acceptance of the $p3 - sm$ series as correct. It seems definitely to show that 35104 does not come into the scheme as the $p_1 2 - s2$ of that system. The $p3 - dm$ set also extrapolate to a $p2 - d2$, which is not that allocated by Carroll and by Paschen if $p_1 2$ is 90660. Also the separation 560 corresponds to a displacement of about $3\frac{1}{4}\delta$, and is thus much less than in the other elements of this group instead of larger. At the same time in themselves they look a good D set, and it cannot be said that they are definitely not. If they are sustained, the 43935 must be removed from the S₂2 list of Part I.—9829.28 becomes $p_1 2 - p_2 2 + s2 - d_1 = s2 - d_1 - 9121.80$, and 9829.67 is the link $p_2(74\frac{1}{2}\delta) - p_1$. The general argument of Part I. is not affected. We must await the determination of its Zeeman pattern.

* Phil. Mag. 4, 1163-5, 1927.

P².

$$55925.33 - 4R/\{m + .180792 + .434404/m\}^2.$$

$$s2 - = 14.476.$$

P(1. *m*).P(2. *m*).

	<i>n.</i>	<i>ν.</i>			
2.	30	60607.58		1 i	-20390.609 †
	50	51484.90	9122.68	1	-29512.602 †
3.	10	111968.6		20	16257.00
	4	108296.3	3672.3	8	12583.62
	3	(530 ± 12)	3439 ± 12		
4.				8 i	32080.721
				2	31227.72
				1n	(28658.67)
					853.00
					3422.05

P(3. *m*).

5.	0	14413.1	25701.8	5 i	40114.394	
				3 i	39752.755	362.14
				4 ii	(36694.251)	3420.64
6.	$\frac{1}{2}$	10912.26	25797	0	44709 ± 10 [6.4] †	
	3	18712.3	200.0		(412286.73)	3423
	1n	10678.4 †	233.9	2n i	44476	† 233
7.	1	21764.3 ⁽¹⁾ †	25798	1 i	47584.83 [62.29] †	
	1	21510.4 †	153.9	0 ii	431.10	† 153.73
				1 i	(160.60)	3424.23
8.	2	23060.3 †	25796.5	1 i	49466.87 [56.21] †	
				1 i	(46048.08)	3148.8

¹ Paschen's *m*=7 is

2 21701.92

1 21542.65 **159.27**

If 14413 is correctly allocated to P(3.5), it gives $s2 - s3 = 25701$, but those for $m=6, 7, 8$ suggest 25798—and then, also, 35106 is not in this series.

S².

$$90661.92, p_1 2 - = 29.881; p^2 2 - = 34.502.$$

$$39297.76, p_1 3 - = 8.527; p_2 3 - = 9.750.$$

$$sm = 4R/\{m + .862651 - .080901/m\}^2.$$

sm—.S(2. *m*).

1.	30	-60607.58	
	50 i	-51484.89	9122.69
			14.476
2.	50 i	35106.14	
	10 i	44228.979	9122.84

S^2 (cont.).

$S(2.m).$			$S(3.m).$		
5.636		51362			
3. 1	60807.80			[9445]	
1	69931.54	9123.74	0	13118	
2.801					
4.			3 ii	(20840.521)	3421.3
			8 i	20588.516	
			6	24261.843	3673.32
			2 ii	(24022.181)	3433.6
1.591					
5.			3	26472.80	
			3 ii	30136.35	3673.55
			1 ii	(26712.686)	3423.69
.9898					
6.			2	29945.72	
			2	33613.61	3667.89
			2 ii	(30183.75)	3429.86
$S(4.m).$					
		15800+			
7. 0	16351	...28		[32179]	
			2 i	35852.308	
8. 4 i	17867.066	...28.5		[33695.59]†	
9. 1	18950.6†	...28.7	1 iii	34772±6	[79.34]†
2 i	19803.1†	853			
10. 4 i	19747.6†	...27	1 ii	35577±6	[74.21]†
	--		1 i	39246.25†	
11. 2 i	20348.9†	...28		[36176.32]	

W. N. in () and † added by W. M. H.

Notes.

$m = 3$. The extrapolated formula for P(3.3) gives $S(3.3) < 9478.55, 13151.87$. Wiedemann has observed 2, 7606, 13144±.8, with which might possibly go McLennan's 2, 10567, 9461.6 sep. 3690±1. Paschen's allocation of [9445] depends on this 3673, which, if the reasoning in the text is accepted, is a doubtful $p3$ doublet.

January 1930.

LXIX. *The Scattering of Sound-Waves by small Elastic Spheres.* By K. F. HERZFELD *.

THE scattering of sound-waves by small spheres has been investigated by Lord Rayleigh †, but only in the case in which the sphere is either liquid or perfectly rigid. In this paper the investigation shall be extended to a solid sphere with finite elastic constants. The first attempt showed a curious difficulty which will be explained first.

The general method to solve such a problem consists in solving separately the equations of motion inside the sphere and in the surrounding liquid. These solutions appear in the form of a progressing series of zonal harmonics, the coefficients of which are functions of the radius vector, and are furthermore multiplied by an indeterminate coefficient. These numerical coefficients are then determined with the help of the surface conditions, considering the factors of each zonal harmonic separately.

In the case of a liquid sphere in another liquid we have one longitudinal wave inside the sphere and one scattered longitudinal wave outside of it (apart from the incident wave, the coefficients of which are known). Accordingly, we have for each zonal harmonic two unknown coefficients which have to be determined by two surface conditions. As such the equality of normal displacements on both sides of the surface, and the equality of normal pressures on both sides of the surface, are chosen, while no account is taken of tangential movement. This latter is justified by the neglect of internal friction. It then turns out that for a small sphere the relative order of magnitude of subsequent coefficients decreases proportionally to $k^2 R_0^2$, where R_0 is the radius of the sphere and k is the propagation constant (2π divided by the wave-length). The two first coefficients are an exception in so far as they are of the same order of magnitude, both proportional to R_0^3 or to the volume of the sphere.

The same holds true for a rigid sphere ‡ where the two

* Communicated by the Author.

† Lord Rayleigh, 'Theory of Sound,' ii. 2nd ed. p. 242 (London, 1896); 'Collected Papers,' i. p. 139. See also H. Lamb, 'Hydrodynamics,' 5th ed. p. 486 (Cambridge, 1924).

‡ The effect of a rigid sphere in a viscous medium has been calculated by Sewell, Phil. Trans. A, ccx. p. 239 (1910). See also Lamb, 'Hydrodynamics,' 5th ed. p. 621.

unknown coefficients are the velocity of the sphere as a whole and the coefficient of the scattered wave. The surface conditions and the statement in respect to the order of magnitude of the coefficients are the same as for a liquid sphere. But if we want now to treat a solid sphere with finite elastic constant, we have one more unknown coefficient, namely inside the sphere the coefficients of the longitudinal and of the transversal waves, and outside the coefficient of the longitudinal wave in the liquid; accordingly we need three surface conditions. If we select then, as was attempted first, the two conditions mentioned before, namely the two recurring to the normal velocity and stress, and in addition the condition of equality of tangential stress on both sides of the surface, it is possible to solve the equations formally; but it turns out that now the second coefficient is no longer of the same order of magnitude of the first one, but subject to the general rule mentioned above, namely smaller by a factor $k^2 R_0^2$.

It was thought that this difficulty, namely that a general elastic sphere should give a result different from the one common to both a liquid and a rigid sphere, was due to a wrong extrapolation (wrong way of passing to the limit), and accordingly it was decided to solve the problem for the quite general case of an elastic sphere in a fluid of moderate viscosity giving now four unknown coefficients, namely the ones for longitudinal and transversal waves in the sphere as well as longitudinal and transverse waves in the liquid, and correspondingly four surface conditions, namely for the normal velocities, the normal pressures, the tangential velocities, and the tangential stresses. It is then found that the difficulty disappears, and if the extrapolation to a non-viscous fluid is performed now, one gets a result in agreement with the cases of the fluid and of the rigid sphere.

The Equations of Motion and their Integration.

The equations of motion of an elastic sphere are given in Love *. Their integration was given by Chree †, who discussed also the free vibrations of such spheres. If we

* A. E. H. Love, 'Treatise on Elasticity,' 3rd ed. Chap. xii. (Cambridge, 1920).

† H. Lamb, Lond. Math. Soc. Proc. vol. xiii. pp. 51, 189 (1882); C. Chree, Camb. Phil. Trans. vol. xiv. p. 50 (1885), vol. xvi. p. 14 (1898).

call v the velocity, we can write the equation of motion in general in the following form :

$$-v = \frac{1}{k_1^2} \text{grad div } v + \frac{1}{k_3^2} (\Delta v - \text{grad div } v). \quad (1)$$

We get this equation from the usual equation of motion which involves the displacement instead of the velocity by assuming the displacement to be proportional to $e^{2\pi i v t}$ and differentiating the whole equation partially in respect to t . Designating the density of the solid by ρ_1 and the elastic constants by λ_1 and μ_1 in the same sense as Love does, k_1 and k_3 have the following meanings :

$$k_1^2 = 4\pi^2 \nu^2 \frac{\rho_1}{\lambda_1 + 2\mu_1}, \quad \dots \quad (2)$$

$$k_3^2 = 4\pi^2 \nu^2 \frac{\rho_1}{\mu_1}. \quad \dots \quad (2')$$

k_1 and k_3 are the propagation constants of the longitudinal (compressional) and transversal (shearing) wave. To integrate equation (1) we proceed following Love and Lamb in the following manner :—We divide the velocity into two parts, $v = v' + v''$. The first part will be due entirely to sources and sinks and will have a velocity potential ψ_1 :

$$\psi_1 = -\frac{1}{k_1^2} \text{div } v, \quad v' = -\text{grad } \psi_1, \quad \dots \quad (3)$$

$$\Delta \psi_1 + k_1^2 \psi_1 = 0; \quad \dots \quad (4)$$

the other part will have no divergence, but is rotatory. We simplify the procedure employed in the books mentioned above by using a method common in electrodynamics *. We introduce a vector Π_3 which is analogous to a Hertz vector in electrodynamics. Owing to the fact that we assume symmetry around the z -axis (the axis of propagation of the plane exciting waves), we get great simplification. Step by step the reasoning is as follows : From $\text{div } v'' = 0$ it follows for (1)

$$\Delta v'' + k_3^2 v'' = 0, \quad \text{or} \quad -\text{rot rot } v'' + k_3^2 v'' = 0.$$

We then write to guarantee the disappearance of $\text{div } v''$:

$$v'' = \text{rot rot } r\Pi_3. \quad \dots \quad (5)$$

The symmetry is insured if we assume the vector Π_3 to have only an r -component (we are going to designate from now

* P. P. Debye, *Ann. d. Phys.* vol. xxx. p. 57 (1909).

on this component simply by Π_3), and not to depend on the geographical length ϕ . It follows, then,

$$\Delta \Pi_3 + k_3^2 \Pi_3 = 0, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$v_r'' = -\frac{1}{r} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \Pi_3}{\partial \theta}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$v_\theta'' = \frac{1}{r} \frac{\partial^2}{\partial \theta \partial r} (r \Pi_3). \quad . \quad . \quad . \quad . \quad . \quad (7')$$

If we now introduce polar coordinates into our Laplacian, and assume again independence of everything from the geographical length, the general solution of the equations (4) and (6) has the form

$$\sum_n a_n \frac{Z_{n+1/2}(kr)}{\sqrt{kr}} P_n(\cos \theta), \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $Z_{n+1/2}(kr)$ is a general cylindrical harmonic of order $n+1/2$ and argument kr , k being either k_1 or k_3 . As the only cylindrical functions which remain finite at the origin are the Bessel functions J , we have to choose them for the inside of the sphere. We introduce the abbreviation

$$I_n(x) = \sqrt{\frac{\pi}{2}} \frac{J_{n+1/2}(x)}{\sqrt{x}}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and write then our solution

$$\psi_1 = \sum A_n I_n(k_1 r) P_n(\cos \theta), \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\Pi_3 = \sum B_n I_n(k_3 r) P_n(\cos \theta). \quad . \quad . \quad . \quad . \quad . \quad (11)$$

In the liquid we can write the equation of motion according to Lamb* quite similar to (1),

$$-v = \frac{1}{k_2^2} \text{grad div } v + \frac{1}{k_4^2} (\Delta v - \text{grad div } v). \quad . \quad . \quad . \quad . \quad (12)$$

In this equation k_2 and k_4 are again the propagation constants of the longitudinal and transversal wave in the liquid. They are determined by the constants of the liquid in a similar manner as (2) and (2'), namely

$$k_2^2 = 4\pi^2 \nu^2 \frac{\rho_2}{\lambda_2 + 4\pi \nu \mu_2}, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$k_4^2 = 2\pi \nu \frac{\rho_2}{\mu_2}. \quad . \quad . \quad . \quad . \quad . \quad (13')$$

* H. Lamb, 'Hydrodynamics,' 5th ed. pp. 547, 611 (Cambridge, 1924).

Here ρ_2 is the density of the liquid, $\frac{1}{\lambda_2}$ the compressibility, and μ_2 the coefficient of internal friction. The only difference compared with (2) and (2') is the appearance of $2\pi\nu\mu_2$ instead of μ_2 . This makes both propagation constants complex, but, as shown by Lamb*, the imaginary part in k_2 is very small for example, for water, while we have for k_4

$$k_4 = \sqrt{2\pi\nu} \sqrt{\frac{\rho_2}{2\mu_2}} (1-i), \dots (13'')$$

and accordingly a very heavy absorption for the transversal waves.

The solution of equation (12) proceeds in a quite analogous way to the solution of (1). We write $v = v' + v''$. v' is determined by the divergence of v and has a velocity potential ψ_2 ,

$$\Delta\psi_2 + k_2^2\psi_2 = 0, \dots (14)$$

$$v' = -\text{grad } \psi_2, \dots (15)$$

while v'' is the rotatory part deducible from a vector Π_4 , for which we get

$$\Delta\Pi_4 + k_4^2\Pi_4 = 0, \dots (16)$$

$$v_r'' = -\frac{1}{r} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial\Pi_4}{\partial\theta}, \dots (17)$$

$$v_\theta'' = \frac{1}{r} \frac{\partial^2}{\partial\theta\partial r} (r\Pi_4). \dots (17')$$

The solution of (14) and (16) will again be of the form (8); but now we have not to select the Bessel function J , as the origin is outside of the region considered, but we have to use the second of the so-called Hankel functions† H , which, at large distance, corresponds to spherical waves travelling outwards. In the case of the transversal waves these will be heavily damped‡. We introduce again an abbreviation analogous to (9):

$$h_n(x) = \sqrt{\frac{\pi}{2}} \frac{H_{n+1/2}(x)}{\sqrt{x}}, \dots (18)$$

and have the solutions of (14) and (16):

$$\psi_2 = \Sigma C_n h_n(k_2 r) P_n(\cos\theta), \dots (19)$$

$$\Pi_4 = \Sigma D_n h_n(k_4 r) P_n(\cos\theta). \dots (20)$$

* *Loc. cit.*

† See, for example, 'H. Bateman, 'Wave-Motion,' Cambridge, p. 37 (1915).

‡ See H. Lamb, 'Hydrodynamics,' p. 586.

We will assume later that kR_0 will be small compared with unity. Accordingly it will be useful to give the power development for the two first functions (9) and (18) :

$$I_0(x) = 1 - \frac{x^2}{6} + \frac{x^4}{120} - \dots, \quad . \quad . \quad . \quad (9')$$

$$I_1(x) = \frac{x}{3} - \frac{x^3}{30} + \frac{x^5}{840} - \dots, \quad . \quad . \quad . \quad (9'')$$

and

$$h_0(x) = i \frac{e^{-ix}}{x} = \frac{i}{x} + 1 - \frac{i}{2}x + \dots, \quad . \quad . \quad . \quad (18')$$

$$h_1(x) = -\frac{e^{-ix}}{x} \left(1 - \frac{i}{x}\right) = -i \frac{d}{dx} \left(\frac{e^{-ix}}{x}\right) = \frac{i}{x^2} \left(1 + \frac{x^2}{2} - \dots\right). \\ . \quad . \quad . \quad (18'')$$

The impinging plane wave has finally a velocity potential

$$\psi_e = e^{-ik_2 z} = e^{-ik_2 r \cos \theta} = \sum (-i)^n (2n+1) I_n(k_2 r) P_n(\cos \theta). \\ . \quad . \quad . \quad (21)$$

The Surface Conditions.

The normal pressure in the solid is given in Love's book *. We can introduce the velocity instead of the displacement by dividing through by $2\pi i\nu$. We find then

$$\begin{aligned} p_{rr} &= \frac{\lambda_1}{2\pi i\nu} \operatorname{div} v + \frac{2\mu_1}{2\pi i\nu} \frac{\partial v_r}{\partial r} = \frac{\lambda_1 + 2\mu_1}{2\pi i\nu} \operatorname{div} v \\ &\quad + \frac{2\mu_1}{2\pi i\nu} \left(-\operatorname{div} v + \frac{\partial v_r}{\partial r} \right) \\ &= 2\pi i\nu \rho_1 \left\{ + \frac{1}{k_1^2} \Delta \psi_1 + \frac{2}{k_3^2} \left(-\Delta \psi_1 + \frac{\partial^2 \psi_1}{\partial r^2} \right. \right. \\ &\quad \left. \left. + \frac{\partial}{\partial r} \frac{1}{r} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \Pi_3}{\partial \theta} \right) \right\} \\ &= -2\pi i\nu \rho_1 \left\{ \psi_1 + \frac{2}{k_3^2} \left(\frac{2}{r} \frac{\partial \psi_1}{\partial r} + \frac{1}{r^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \psi_1 \right. \right. \\ &\quad \left. \left. - \frac{\partial}{\partial r} \frac{1}{r} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \Pi_3}{\partial \theta} \right) \right\}. \quad (22) \end{aligned}$$

Here repeated use has been made of (4).

* See Love, 'Elasticity,' p. 284.

In the liquid the tensions are given in Lamb's book on p. 602. To eliminate the pressure p , we make use of the following formula:—

$$p = \frac{1}{2\pi\nu} \frac{\partial p}{\partial t} = \frac{1}{2\pi\nu} \frac{\lambda_2}{\rho_2} \frac{\partial \rho}{\partial t} = -\frac{\lambda_2}{2\pi\nu} \operatorname{div} v.$$

It then turns out that the normal tension p_{rr} takes the same form as in the solid (22), with the exception already noted in (13') that $2\pi\nu\mu_2$ takes the place of μ_1 . Accordingly we can write after the same transformations which were performed in (22)

$$p_{rr} = -2\pi\nu\rho_2 \left\{ \psi_2 + \psi_e + \frac{2}{k_4^2} \left(\frac{2}{r} \frac{\partial(\psi_2 + \psi_e)}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial(\psi_2 + \psi_e)}{\partial \theta} - \frac{\partial}{\partial r} \frac{1}{r} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \Pi_4}{\partial \theta} \right) \right\}. \quad \dots (23)$$

The surface condition as to the normal pressures consists in putting (22) equal to (23).

The tangential stress in the solid is expressed in terms of the displacement, instead of which we can introduce $\frac{v}{2\pi\nu}$.

Then the tangential stress takes the form

$$\begin{aligned} & \frac{\mu_1}{2\pi\nu} \left(\frac{\partial v_r}{\partial \theta} + r^2 \frac{\partial}{\partial r} \frac{v_\theta}{r} \right) \\ &= -\frac{\mu_1}{2\pi\nu} \frac{\partial}{\partial \theta} \left\{ \frac{\partial \psi_1}{\partial r} + r^2 \frac{\partial}{\partial r} \frac{\psi_1}{r^2} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \Pi_3}{\partial \theta} - r^2 \frac{\partial}{\partial r} \frac{1}{r^2} \frac{\partial r \Pi_3}{\partial r} \right\} \\ &= -2 \frac{\mu_1}{2\pi\nu} \frac{\partial}{\partial \theta} \left\{ r \frac{\partial}{\partial r} \left(\frac{\psi_1}{r} \right) + \frac{\partial \Pi_3}{\partial r} + \frac{\Pi_3}{r} \left(1 + \frac{k_3^2 r^2}{2} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \Pi_3}{\partial \theta} \right\}. \quad \dots (24) \end{aligned}$$

The same formula is valid for this liquid, except for the replacement of μ_1 by $2\pi\nu\mu_2$. The surface condition then takes the form

$$\rho_1 k_4^2 \left(\frac{\partial v_r}{\partial \theta} + r^2 \frac{\partial}{\partial r} \frac{v_\theta}{r} \right)_{\text{solid}} = \rho_2 k_3^2 \left(\frac{\partial v_r}{\partial \theta} + r^2 \frac{\partial}{\partial r} \frac{v_\theta}{r} - r \frac{\partial}{\partial r} \frac{\psi_e}{r} \right)_{\text{liquid}} \quad \dots (25)$$

Finally, we have the condition of equal radial velocity

$$\frac{\partial \psi_1}{\partial r} - \frac{1}{r} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \Pi_3}{\partial \theta} = \frac{\partial (\psi_2 + \psi_e)}{\partial r} - \frac{1}{r} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \Pi_4}{\partial \theta} \quad (26)$$

and equal tangential velocity

$$\frac{1}{r} \frac{\partial}{\partial \theta} \psi_1 + \frac{1}{r} \frac{\partial^2}{\partial \theta \partial r} (r \Pi_3) = \frac{1}{r} \frac{\partial}{\partial \theta} (\psi_2 + \psi_e) + \frac{1}{r} \frac{\partial^2}{\partial \theta \partial r} (r \Pi_4). \quad (27)$$

We introduce now the development (10), (11), (19), (20), (21), make use of the differential equation of the zonal harmonics

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} P_n = -n(n+1) P_n,$$

and equal the coefficients of each zonal harmonic. We find then, for the surface conditions, if a dash denotes differentiation in respect to the argument,

$$\begin{aligned} \frac{\rho_1}{\rho_2} A_n \left[\left(1 - \frac{2n(n+1)}{k_3^2 r^2} \right) I_n(k_1 r) + 4 \frac{k_1}{k_3} \frac{1}{k_3 r} I_n'(k_1 r) \right] \\ + 2 \frac{\rho_1}{\rho_2} n(n+1) B_n \frac{d}{dk_3 r} \frac{I_n(k_3 r)}{k_3 r} \\ = C_n \left[\left(1 - \frac{2n(n+1)}{k_4^2 r^2} \right) h_n(k_2 r) + 4 \frac{k_2}{k_4} \frac{1}{k_4 r} h_n'(k_2 r) \right] \\ + 2n(n+1) D_n \frac{d}{dk_4 r} \frac{h_n(k_4 r)}{k_4 r} \\ + (-1)^n (2n+1) \left[\left(1 - \frac{2n(n+1)}{k_4^2 r^2} \right) I_n(k_2 r) \right. \\ \left. + 4 \frac{k_2}{k_4} \frac{1}{k_4 r} I_n'(k_2 r) \right], \quad (23') \end{aligned}$$

$$\begin{aligned} \frac{\rho_1}{\rho_2} \frac{k_4^2}{k_3^2} A_n r^2 \frac{d}{dr} \frac{I_r(k_1 r)}{r} \\ + B_n \frac{\rho_1}{\rho_2} \frac{k_4^2}{k_3^2} \left[\frac{d}{dr} (r I_n(k_3 r)) - \left(n(n+1) - \frac{k_3^2 r^2}{2} \right) I_n(k_3 r) \right] \\ = C_n r^2 \frac{d}{dr} \left[\frac{h_n(k_2 r)}{r} \right] + D_n \left[\frac{d}{dr} (r h_n(k_4 r)) \right. \\ \left. - \left(n(n+1) - \frac{k_4^2 r^2}{2} \right) h_n(k_4 r) \right] \\ + (-1)^n (2n+1) r^2 \frac{d}{dr} \left(\frac{I_n(k_2 r)}{r} \right), \quad (25') \end{aligned}$$

except for $n=0$.

$$\begin{aligned} k_1 A_n I_n'(k_1 r) - n(n+1) k_3 B_n \frac{I_n(k_3 r)}{k_3 r} \\ = k_2 C_n h_n'(k_2 r) - n(n+1) D_n k_4 \frac{h_n(k_4 r)}{k_4 r} \\ + (-1)^n (2n+1) k_2 I_n'(k_2 r), \quad \dots \quad (26') \end{aligned}$$

$$\begin{aligned} A_n I_n(k_1 r) - B_n \frac{d}{dr} [r I_n(k_3 r)] \\ = C_n h_n(k_2 r) - D_n \frac{d}{dr} [r h_n(k_4 r)] \\ + (-1)^n (2n+1) I_n(k_2 r), \quad \dots \quad (27') \end{aligned}$$

except for $n=0$. In all these formulas there has to be substituted $r=R_0$, the radius of the sphere. As the coefficients of the development (21) are all of the same order of magnitude, while for $kR_0 < 1$ the relative order of magnitude of two consecutive functions I_n and I_{n+1} is proportional to kR_0 , the relative order of magnitude of two subsequent functions h_n and h_{n+1} is proportional to $\frac{1}{kR_0}$. The statement made on p. 740 concerning the relative order of magnitude of consecutive coefficients can easily be verified, except in the case $n=0$ in relation to $n=1$.

The Coefficients of the Scattered Wave.

In the evaluation of the equations (25') to (27') we shall limit ourselves for the sake of simplicity to small spheres so that $k^2 R_0^2$ will be neglected in comparison with unity. This means that for spheres of diameter 0.1 mm. radius and a frequency of 300 kilocycles (about 5 mm. wave-lengths) we make an error of about 1 per cent. An exception will be made for $k_4 R_0$, as this might not be small for high frequencies in water. On account of the complex character of k_4 we will keep

$$e^{-\iota k_4 R_0} = e^{-\frac{|k_4|}{\sqrt{2}} R_0} e^{-\frac{|k_4|}{\sqrt{2}} \iota R_0}$$

without making a Taylor development. We then find for $n=0$

$$\begin{aligned} \frac{\rho_1}{\rho_2} A_0 \left(1 - \frac{4}{3} \frac{k_1^2}{k_2^2}\right) = \frac{C_0 \iota}{k_2 R_0} \left(1 - \iota k_2 R_0 - \frac{4k_2^2}{k_4^2} \frac{1}{k_2^2 R_0^2}\right) \\ + \left(1 - \frac{4}{3} \frac{k_2^2}{k_4^2}\right), \quad \dots \quad (23'') \end{aligned}$$

$$-k_1 A_0 \frac{k_1 R_0}{3} = -k_2 \frac{C_0 \iota}{k_2^2 R_0^2} - \frac{1}{3} k_2 \cdot k_2 R_0, \quad \dots \quad (26'')$$

Therefore

$$C_0 = -\epsilon \frac{k_2^3 R_0^3}{3} \frac{\frac{\rho_2}{\rho_1} \frac{k_1^2}{k_2^2} - 1 + \frac{4}{3} \frac{k_1^2}{k_3^2} \left(1 - \frac{\rho_2}{\rho_1} \frac{k_3^2}{k_4^2}\right)}{1 - \frac{4}{3} \frac{k_1^2}{k_2^2} \left(1 - \frac{\rho_2}{\rho_1} \frac{k_3^2}{k_4^2}\right)}. \quad (28)$$

Furthermore, we get for $n=1$

$$\begin{aligned} & \frac{\rho_1}{\rho_2} \frac{A_1}{3} k_1 R_0 \left[1 - \frac{4}{5} \frac{k_1^2}{k_3^2} \right] - \frac{4}{15} \frac{\rho_1}{\rho_2} B_1 k_3 R_0 \\ &= \frac{C_1 \iota}{k_2^2 R_0^2} \left[1 - 2 \frac{k_2^2}{k_4^2} - \frac{12}{k_4^2 R_0^2} \right] \\ & \quad - \frac{12 \iota D_1}{k_4^2 R_0^2} e^{-\iota k_4 R_0} \left[\frac{1 + \iota k_4 R_0}{k_4^2 R_0^2} - \frac{1}{3} \right] - 3 \iota \frac{k_2 R_0}{3} \left(1 - \frac{4}{5} \frac{k_2^2}{k_4^2} \right), \end{aligned} \quad \dots (23''')$$

$$\begin{aligned}
 & -\frac{k_4^2}{k_3^2} \frac{\rho_1}{\rho_2} A_1 \frac{k_1^3 R_0^3}{15} + \frac{k_4^2}{k_3^2} \frac{\rho_1}{\rho_2} B_{110} k_3^3 R_0^3 \\
 & = -\frac{3C_1}{k_2^2 R_0^2} (1 + \frac{1}{6} k_2^2 R_0^2) \\
 & \quad - \frac{3D_1 e^{-ik_4 R_0}}{k_4^2 R_0^2} (1 + ik_4 R_0 - \frac{1}{2} k_4^2 R_0^2) + 3i \frac{k_2^3 R_0^3}{15},
 \end{aligned}$$

$$\begin{aligned}
 k_1 A_1 \left(\frac{1}{3} - \frac{k_1^2 R_0^2}{10} \right) - 2k_3 B_1 \left(\frac{1}{3} - \frac{k_3^2 R_0^2}{30} \right) \\
 = -2i \frac{k_2 C_1}{k_2^3 R_0^3} - 2i \frac{D_1 k_4 e^{-ik_4 R_0}}{k_4^3 R_0^3} (1 + ik_4 R_0) \\
 - 3ik_2 \left(\frac{1}{3} - \frac{k_2^2 R_0^2}{10} \right), \quad \dots \quad (26''')
 \end{aligned}$$

$$\begin{aligned} & A_1 k_1 R_0 \left(\frac{1}{3} - \frac{k_1^2 R_0^2}{30} \right) - 2 B_1 k_3 R \left(\frac{1}{3} - \frac{k_3^2 R_0^2}{15} \right) \\ &= \frac{C_1 \iota}{k_2^2 R_0^2} \left(1 + \frac{k_2^2 R_0^2}{2} \right) + \frac{D_1 \iota}{k_4^2 R_0^2} e^{-\iota k_4 R_0} [1 + \iota k_4 R_0 - k_4^2 R_0^2] \\ &\quad - 3 \iota k_2 R_0 \left(\frac{1}{3} - \frac{k_2^2 R_0^2}{30} \right). \quad \cdot \quad \cdot \quad (27''') \end{aligned}$$

On the right-hand side of (23''') and (25''') we had to go to the next higher power in the development of h_1 , and on the left-hand side of (26'') and (26''') to the next higher power in the development of I_1 on account of $k^2 R_0^2$ in the denominator, so that the resultant formulas will be accurate within the limit stated on p. 749.

Subtracting (27''') from (26''') we find

$$\frac{3\iota}{k_2^3 R_0^3} \left\{ C_1 \left(1 + \frac{k_2^2 R_0^2}{6} \right) + D_1 \frac{k_2^2}{k_4^2} \left(1 + \iota k_4 R_0 - \frac{k_4^2 R_0^2}{3} \right) e^{-\iota k_4 R_0} \right\} \\ = \frac{k_2^2 R_0^2}{5} \left(\frac{k_1^3}{k_2^3} \frac{A_1}{3} + \frac{k_3^3}{k_2^3} \frac{B_1}{3} + \iota \right),$$

where higher powers in kR_0 are necessary for the solution of (23''') and (25'''). Introducing this equation into (23''') and (25''') leads to

$$\frac{k_1}{k_2} \frac{A_1}{3\iota} \left[\frac{\rho_1}{\rho_2} + \frac{4}{5} \left(\frac{k_1^2}{k_4^2} - \frac{\rho_1}{\rho_2} \frac{k_1^2}{k_3^2} \right) \right] + \frac{4}{15} \frac{k_3}{k_2} \frac{B_1}{\iota} \left(\frac{k_3^2}{k_4^2} - \frac{\rho_1}{\rho_2} \right) = \frac{C_1}{k_2^3 R_0^3} - 1, \quad (23''''')$$

$$\frac{k_1}{k_2} \frac{A_1}{3\iota} \left(\frac{k_1^2}{k_4^2} - \frac{\rho_1}{\rho_2} \frac{k_1^2}{k_3^2} \right) + \frac{k_3}{k_2} \frac{B_1}{3\iota} \left(\frac{k_3^2}{k_4^2} + \frac{3}{2} \frac{\rho_1}{\rho_2} \right) = -\frac{5}{2} \frac{C_1}{k_2^3 R_0^3}. \quad (25''''')$$

These, when subtracted, give

$$\frac{k_1}{k_2} \frac{A_1}{3\iota} \frac{\rho_1}{\rho_2} - 2 \frac{k_3}{k_2} \frac{B_1}{3\iota} \frac{\rho_1}{\rho_2} = 3 \frac{C_1}{k_2^3 R_0^3} - 1,$$

while the lowest order in (26''') can be written

$$\frac{k_1}{k_2} \frac{A_1}{3\iota} - 2 \frac{k_3}{k_2} \frac{B_1}{3\iota} = -1.$$

This finally leads to the solution

$$C_1 = k_2^3 R_0^3 \frac{\rho_2 - \rho_1}{3\rho_2}, \quad (29)$$

$$D_1 e^{-\iota k_4 R_0} = -k_2 k_4^2 R_0^3 \frac{\rho_2 - \rho_1}{3\rho_2} \frac{1}{1 + \iota k_4 R_0}, \quad (29')$$

with an accuracy sufficient for the calculation of the scattered wave. This is then given by

$$\psi_2 = \frac{k_2^2 R_0^3}{3} \frac{\rho_2}{\rho_1} \frac{k_1^2}{k_2^2} - 1 + \frac{4}{3} \left(\frac{k_1^2}{k_3^2} - \frac{\rho_2}{\rho_1} \frac{k_1^2}{k_4^2} \right) \frac{e^{-\iota k_2 r}}{r} \\ 1 - \frac{4}{3} \left(\frac{k_1^2}{k_3^2} - \frac{\rho_2}{\rho_1} \frac{k_1^2}{k_4^2} \right) \\ + \frac{k_2^2 R_0^3}{3} \frac{\rho_2 - \rho_1}{\rho_2} \frac{e^{-\iota k_2 r}}{r} \left(1 - \frac{\iota}{k_2 r} \right) \cos \theta. \quad (30)$$

$$\Pi_4 = - \frac{k_2 k_4 R_0^3}{1 + \iota k_4 R_0} \frac{\rho_2 - \rho_1}{\rho_1} e^{-\iota k_4 (r - R_0)} \left(1 - \frac{\iota}{k_4 r} \right) \cos \theta. \quad (31)$$

LXX. *Propagation of Sound in Suspensions.*

By K. F. HERZFELD *.

Introduction.

THE development of the sonic interferometer by Hubbard and Loomis † has made possible a very precise measurement of the velocity of sound in liquids, and this can be used to calculate with high accuracy the compressibility of liquids. The measurement of the compressibility of solids, on the other hand, which is of great importance for our knowledge of the molecular forces, needs quite an elaborate experimental equipment ‡. It would be of great advantage if the same method (sonic interferometer with piezo-electric quartz as source) could be used. It was therefore thought possible to measure the velocity of sound in suspensions of small particles, the compressibility of which should be investigated, in a liquid for which the velocity of sound could be determined separately.

In fact, it had been observed previously that the pitch of a liquid column changes when a granular deposit is stirred up §, but no quantitative theory existed. In giving here the theory, we do not distinguish between adiabatic and isothermal compression. In solids the difference is small. Furthermore, we neglect any influence of a change in temperature which might occur in the suspension through conduction from the liquid which, compressed adiabatically, will undergo small periodic temperature changes.

We will assume that the particles are small spheres, and we will treat them as isotropic solids, assuming that this will be a fair average of the effect of the random orientation of anisotropic particles.

There are two methods to calculate the velocity of propagation as influenced by obstacles. We will first describe one which best gives the physical meaning, but is only suited for a first approximation, and then proceed with a method necessary for higher approximations, but less clear.

* Communicated by the Author.

† J. C. Hubbard and A. L. Loomis, *Phil. Mag.* v. p. 1177 (1928); A. L. Loomis and J. C. Hubbard, *Journ. Amer. Opt. Soc.* xvii. p. 295 (1928).

‡ See, for example, T. W. Richards, *Carnegie Inst. Wash.* No. 76, 1907; E. Madelung und R. Fuchs, *Ann. d. Phys.* lxx. p. 289 (1921).

§ Unpublished observation of J. C. Hubbard.

Calculation of the Velocity in Suspensions.
First Approximation.

The idea of this method is due to Lord Rayleigh*, and consists in the following:—

If a plane wave (the primary wave) falls on a small object, this object will emit a scattered wave which, at large distances, will die out. If we have now a layer of thickness dz containing N of the obstacles per cub. cm., and extending to infinity in a plane at right angles to the direction of propagation of the primary beam (z -direction), the scattered waves from all these obstacles will compound at a large distance from the layer to two plane waves of the same frequency as the primary wave, one going in the opposite direction (reflected wave from the layer), the other going in the same direction as the primary beam. The latter, together with the primary wave, will give a resultant wave, which will have a phase difference proportional to dz compared with the primary wave. This will amount to the same thing as if the primary wave had a different velocity of propagation in the layer dz .

In the case of the first approximation, with which we are dealing now, we can describe the motion in the liquid by a velocity potential ψ , so that the velocity is given by

$$v = -\text{grad } \psi. \quad (32)$$

The primary wave will have a velocity potential equal to

$$\psi_0 = e^{2\pi i\nu \left(t - \frac{z}{V_0}\right)}. \quad (33)$$

We write now the velocity potential of the plane wave compounded from the scattered waves:

$$\psi' = A_1 dz e^{2\pi i\nu \left(t - \frac{z}{V_0}\right)}. \quad (34)$$

We want the resultant wave, the velocity potential of which will be equal to $\psi_0 + \psi'$, equivalent to a wave which has had a different velocity V in the layer dz , and which, therefore, has a velocity potential

$$\psi = e^{2\pi i\nu \left(t - \frac{z-dz}{V_2} - \frac{dz}{V}\right)} = e^{2\pi i\nu \left(t - \frac{z}{V_2}\right)} \left(1 + 2\pi i \left(1 - \frac{V_2}{V}\right) \frac{dz}{\lambda}\right),$$

* Lord Rayleigh, *Phil. Mag.* (5) xlvii. p. 375 (1899); 'Collected Papers,' iv. p. 397. See also K. F. Herzfeld, *Zeit. f. Phys.* xxiii. p. 341 (1924).

where $\lambda = \frac{V}{\nu}$ is the wave-length. From this it follows

$$1 - \frac{V_2}{V} = \frac{\lambda}{2\pi} A. \quad . \quad . \quad . \quad . \quad (35)$$

In our particular case the velocity potential of a wave scattered by a fluid sphere of density ρ_1 and compressibility K_1 in a liquid of density ρ_2 and compressibility K_2 is * (R_0 radius of the sphere):

$$\psi'' = \frac{4\pi^2 R_0^3}{3\lambda^2 r} \left(\frac{K_1 - K_2}{K_1} + 3 \frac{\rho_2 - \rho_1}{\rho_2 + 2\rho_1} \cos \theta \right) e^{2\pi i \nu \left(t - \frac{r}{V_2} \right)}. \quad (36)$$

We have to integrate this over an infinite surface in the xy plane. The first part of our expression gives directly a plane wave (containing z only in the form 2). The next member gives, besides a plane wave, additional terms with powers of z in the denominator, which therefore die out at great distances. If we introduce the abbreviation

$$\beta = N \frac{4\pi R_0^3}{3}$$

which gives the fraction of space filled by the particles, we find then from equation (35)

$$- \frac{V - V_2}{V} = \frac{\beta}{2} \left(\frac{K_1 - K_2}{K_1} + 3 \frac{\rho_1 - \rho_2}{\rho_2 + 2\rho_1} \right). \quad . \quad . \quad (37)$$

If we compare this with the result which we should get in a uniform medium having a compressibility $K_2 + \beta(K_1 - K_2)$ and a uniform density $\rho_2 + \beta(\rho_1 - \rho_2)$, namely

$$- \frac{V - V_2}{V} = \frac{\beta}{2} \left(\frac{K_1 - K_2}{K_2} + \frac{\rho_1 - \rho_2}{\rho} \right), \quad . \quad . \quad (37')$$

we see that the first member is identical, while the second agrees only if the difference in density is small.

In the preceding calculation we have used only the first member in the series which gives the scattered wave.

This means that we have neglected $\left(\frac{R_0}{\lambda} \right)^2$ compared with unity. In this case only the total volume β enters, not the radius explicitly. We are going to use the same approximation for solid spheres, and may hope that then the formula will be applicable also if the particles are not exactly

* Lord Rayleigh, 'Theory of Sound,' 2nd ed. ii. p. 284 (London, 1896).

spheres, as only the total volume of the suspended material matters.

Furthermore, we have taken into account only uniform expansions of this sphere and motions of the sphere as a whole, but neglected all shearing and frictional effects. As explained in the preceding paper, we have to proceed in a different manner for a solid sphere. The introduction of (30) and (30') of the preceding paper, instead of (36) into (35) then leads to the following formula for the propagation of a sound-wave through a suspension of solid spheres:—

$$\frac{V_2 - V}{V} = \frac{\beta}{2} \left[\frac{\rho_2 k_1^2}{\rho_1 k_2^2} \frac{1}{1 - \frac{4}{3} \frac{k_1^2}{k_3^2}} - 1 + \frac{\rho_1 - \rho_2}{\rho_2} \right]. \quad (38)$$

Here, only the longitudinal waves have been taken into account, as the transversal waves in the liquid die out so rapidly that they do not contribute to the wave-front of the secondary wave at a great distance. The absorption of energy, for which they are responsible, is taken care of in the imaginary parts of the longitudinal waves, the amplitudes of which are influenced by the presence of the transversal waves in the surface condition. In formula (38) only the real parts of the amplitudes of the longitudinal waves have been taken in, and $\frac{k_1^2}{k_4^2}$ and $\frac{k_2^2}{k_4^2}$ have been neglected compared with unity.

Furthermore, the mutual influence that the suspended particles have on each other has been neglected in the calculation for both liquid and solid suspension. One part of this influence could easily be taken into account*, namely the influence of the reflected wave on preceding layers.

This would substitute for $\frac{V - V_2}{V_2}$ the expression $\frac{V^2 - V_2^2}{2V_2^2}$,

corresponding in optics to the change from $n-1$ to $\frac{n^2-1}{2}$.

But we have, besides, to consider the analogy of the Lorenz-Lorentz force in optics, and to do this a more complicated method is necessary.

If we now introduce the values of k_1^2 and k_3^2 from (2) and (2'), introduce the cubical compressibility of the solid

$$\frac{1}{K_1} = \lambda_1 + \frac{2}{3}\mu_1,$$

* P. P. Ewald, *Physica*, iv. p. 234 (1924).

and finally substitute for k_2^2 its value (13), neglecting as before the imaginary part, the expression appearing in the bracket of (38) becomes

$$\frac{\rho_2 k_1^2}{\rho_4 k_2^2} \frac{1}{1 - \frac{4}{3} \frac{k_1^2}{k_3^2}} = \frac{\lambda_2}{\lambda_1 + 2\mu_1} \frac{1}{1 - \frac{4}{3} \frac{\mu_1}{\lambda_1 + 2\mu_1}} = \frac{\lambda_2}{\lambda_1 + \frac{2}{3}\mu_1} = \frac{K_1}{K_2},$$

and (38) takes the form

$$\frac{V_2 - V}{V} = \frac{\beta}{2} \left(\frac{K_1 - K_2}{K_2} + \frac{\rho_1 - \rho_2}{\rho_2} \right), \quad . \quad . \quad (38')$$

which is identical with (37').

Ewald's Method.

Outline of the Method.

To make the rather complicated calculation which will follow a little more clear, we give first an example of Ewald's method* in the simplest case. Assume that we have a medium filled with N oscillators per cu. cm. These oscillators shall give a scattered wave of the simplest type (spherical symmetry, as in the case of an expanding sphere). We put the velocity potential of the scattered wave equal to

$$\psi'' = a\psi_0 e^{2\pi i v t - i k_2 r}$$

if the velocity potential of the primary wave has the amplitude ψ_0 . In this formula k_0 means the "propagation constant" = $\frac{2\pi}{\lambda_2}$, where λ_2 is the wave-length in the empty medium (without oscillators).

We now want to set up a state of motion in which the oscillators oscillate at a given frequency, and the phase of the oscillators proceeds in the form of a plane wave along the direction z . We call the propagation constant of this oscillator phase $k = \frac{2\pi}{\lambda}$, where λ would then be the wave-length of the oscillator phase, or the wave-length of the gross disturbance, or the quantity which we should measure as wave-length in the medium filled with oscillators.

* P. P. Ewald, Thesis (Münich, 1912); *Ann. d. Phys.* xlix. pp. 1, 117 (1916). See also a number of papers by L. Natanson in *Bull. Acad. Sci. Crak.* C. G. Darwin, *Trans. Camb. Phil. Soc.* xxiii. p. 137 (1924).

If we are deep in the medium, the disturbance will be made up entirely from the mutual radiation of the oscillators, the primary beam having been lost in surface-layers. We know, therefore, on the one hand, that the disturbance is given by the plane wave which has, at the point z' , the velocity potential

$$\psi = \psi_0 e^{2\pi i \nu t - k z'}.$$

On the other hand, this must be made up by contributions from all oscillators, and therefore be equal to

$$\begin{aligned} \psi &= a N \psi_0 e^{2\pi i \nu t} \int \frac{e^{-i k_0 r - i k z}}{r} 2\pi r^2 dr d\theta \\ &= 2\pi N a e^{2\pi i \nu t - k z'} \int \frac{e^{-i k_0 r - i k r \cos \theta}}{r} 2\pi r^2 dr d\theta \\ &\quad (z = z' + r \cos \theta). \end{aligned}$$

This leads to the equation of dispersion

$$1 = \frac{4\pi N a}{k_0^2 - k^2},$$

defining the propagation constant k and therefore the velocity of the resultant wave in agreement with a direct calculation by the method mentioned before.

The Exciting Field.

To calculate the exciting field on the surface of one particle, we have to sum up the contributions of all other particles, which we assume uniformly distributed over the medium, substituting an integration for the summation. The task would be very simple if we could assume the other particles to be present everywhere (integration over the whole space). Instead, we have to consider that the centre of no other particle can be inside a sphere of radius $2R_0$ around the centre of the considered particle. Accordingly we have to subtract from the previous integral (which in optics is analogous to the electric field) the contributions which would come from particles contained in the sphere $2R_0$ (this corresponds in optics to the negative Lorentz-Lorenz force, leaving finally after subtraction the exciting force).

In principle these will be contributions to the exciting field from both the longitudinal and the transversal waves; but here, too, as in the preceding paper, we shall neglect the

contributions of the transversal waves. From what we have just explained, it can be seen that only waves coming from a distance farther than $2R_0^2$ to the surface of the considered sphere (that means waves which will have travelled at least the distance R_0) will contribute to the exciting field. If we now assume that $k_4 R_0$ is large compared with unity, as it will be for high-frequency sound-waves in water, and particles not much smaller than 0.01 mm., the absorption of the transversal waves will be sufficient to make them negligible. Accordingly, the exciting field will be calculated from the longitudinal waves alone.

We want first to show that it is possible to get the exciting velocity from an exciting potential ψ_e . We call the place where we want to calculate the velocity x, y, z , the place of the particle acting as source ξ, η, ζ . If we have N particles per cm.³, the particles in $d\xi, d\eta, d\zeta$ give a velocity in x, y, z :

$$v_x = -\frac{\partial}{\partial x} \psi_2 \cdot N d\xi d\eta d\zeta e^{-ikz},$$

as we have assumed that there is an "oscillator wave" proceeding through the medium proportional to e^{-ikz} , giving a corresponding phase-factor. In ψ_2 the argument is

$$r = \sqrt{(x-\xi)^2 + (y-\eta)^2 + (z-\zeta)^2}, \quad \cos \vartheta = \frac{z-\zeta}{r}.$$

Therefore the resultant velocity is

$$v_x = -N \iiint e^{-ikz} \frac{\partial \psi_2}{\partial x} d\xi d\eta d\zeta = -\frac{\partial \psi_e}{\partial x}, \quad (39)$$

$$\psi_e = N \iiint e^{-ikz} \psi_2 d\xi d\eta d\zeta. \quad (40)$$

We then divide ψ_e into two parts, ψ_e' being calculated by integration over the whole space from which ψ_e'' , the contribution of a sphere of radius $2R_0$ around the centre of the considered particle, has to be subtracted:

$$\psi_e = \psi_e' - \psi_e''. \quad (41)$$

In the calculation of ψ_e' we introduce polar coordinates R, Θ, Φ around the point of observation x, y, z . We write

$$e^{-ikz} = e^{-ikz} e^{-ik(\zeta-z)} = e^{-ikz} e^{-ikR \cos \Theta}.$$

Here we have made use of the fact that $r=R$, while ϑ (the angle r makes with the z -axis measured in the place of the

particle) is $\pi - \Theta$, where Θ is the angle r (or R) makes with the z -axis in the observation point. (40) then takes the form

$$\psi_e' = N e^{-i k z} 2\pi \iint e^{-i k R \cos \Theta} \psi_2 R^2 dR \sin \Theta d\Theta.$$

In this we introduce (19) and (21), make use of the well-known formulas

$$\int P_n P_m \sin \Theta d\Theta = 0 \quad n \neq m, \quad \int P_n^2 \sin \Theta d\Theta = \frac{2}{2n+1},$$

and remember that

$$P_n(\cos \theta) = (-1)^n P_n(\cos \Theta).$$

We then find

$$\psi_e' = N e^{-i k z} \sum C_n \alpha_n(k_2 k) \quad . \quad . \quad . \quad (41)$$

with *

$$\begin{aligned} \alpha_n(k_2, k) &= 4\pi \iota^n \int_0^\infty I_n(kR) h_n(k_2 R) R^2 dR \\ &= 2\pi^2 \iota^n \int \frac{J_{n+\frac{1}{2}}(kR) H_{n+\frac{1}{2}}(k_2 R)}{R k_2} R dR \\ &= \frac{2\pi^2 \iota^n}{\sqrt{k_2 k (k_2^2 - k^2)}} \left[R \{ k_2 H_{n+\frac{1}{2}}(k_2 R) J_{n+\frac{1}{2}}(kR) \right. \\ &\quad \left. - k H_{n+\frac{1}{2}}(k_2 R) J_{n+\frac{1}{2}}(kR) \} \right]_0^\infty \\ &= - \frac{4\pi}{\sqrt{k_2 k (k_2^2 - k^2)}} \iota^{n+1} \left(\frac{k}{k_2} \right)^{n+\frac{1}{2}} = - \frac{4\pi}{k_2} \frac{\iota^{n+1}}{k_2^2 - k^2} \left(\frac{k}{k_2} \right)^n. \end{aligned} \quad . \quad . \quad . \quad (42)$$

Here $\lim_{R \rightarrow \infty} e^{i(k-k_2)R}$ has to be neglected, as is the case also in Ewald's work, as otherwise the particular form of the outward boundary would play a rôle (give a diffraction pattern). Re-writing (41) we get finally for the first part of the exciting field

$$\begin{aligned} \psi_e' &= \frac{3\beta}{k_2^3 R_0^3} \frac{k_2^2 \iota}{k^2 - k_2^2} \sum C_n \iota^n \left(\frac{k}{k_2} \right)^n \\ &\quad \times \sum (-\iota)^m (2m+1) I_m(kR) P_m(\cos \Theta). \end{aligned} \quad (43)$$

* See, for example, P. Schafheitlin, 'Theorie der Besselschen Funktionen,' p. 68 (Leipzig, 1908).

The calculation of ψ_e'' is much more complicated on account of the finiteness of the limits in the integral. If we call, as before, ξ, η, ζ the position of the source, x, y, z the point at which the potential has to be calculated, x_0, y_0, z_0 the centre of the sphere for the surface of which we want to calculate the exciting radiation, we have to introduce polar coordinates around this centre :

$$R^2 = (\xi - x_0)^2 + (\eta - y_0)^2 + (\zeta - z_0)^2,$$

$$R \cos \Theta = \zeta - z_0.$$

The expressions r and θ , which appear in the formula (19) of ψ_2 , have, on the other hand, the meaning

$$r^2 = (x - \xi)^2 + (y - \eta)^2 + (z - \zeta)^2,$$

$$r \cos \theta = \zeta - z.$$

Our task is then the evaluation of

$$\begin{aligned} \psi_e'' &= N e^{-ikz_0} \int_0^{2R_0} \int_0^\pi \int_0^{2\pi} e^{-ik(\zeta - z_0)} \psi_2 d\Phi \sin \Theta d\Theta R^2 dR \\ &= \frac{3}{4\pi} \beta \frac{e^{-ikz_0}}{R_0^3} \int_0^{2R_0} \int_0^\pi \int_0^{2\pi} e^{-ik(\zeta - z_0)} [C_0 h_0(k_2 r) \\ &\quad + C_1 h_1(k_2 r) P_1(\cos \theta) \dots] R^2 dR \sin \Theta d\Theta d\Phi. \quad (44) \end{aligned}$$

As before, we restrict our calculations to members larger than $k^2 R_0^2$. Accordingly we develop h_0 and the ρ power. Furthermore, we make use of the formula following from (18') and (18'') :

$$h_1(kr) \cos \theta = \frac{\partial r}{\partial z} h_1(kr) = \frac{\partial r}{\partial z} \left(-\frac{dh_0(kr)}{dkr} \right) = -\frac{\partial}{\partial kz} h_0(kr).$$

Accordingly we can re-write (44) in the following manner :

$$\begin{aligned} \psi_e'' &= \frac{3}{4\pi} \beta \frac{e^{-ikz_0}}{R_0^3} \left(C_0 - C_1 \frac{\partial}{\partial k_2 z} \right) \\ &\quad \times \int_0^{2R_0} \int_0^\pi \int_0^{2\pi} \left[1 - ik(\zeta - z_0) - \frac{k^2}{2} (\zeta - z_0)^2 - \dots \right] \\ &\quad \left[\frac{\iota}{k_2 r} + 1 - \frac{\iota k_2 r}{2} + \dots \right] R^2 dR \sin \Theta d\Theta d\Phi \\ &= \frac{3}{4\pi} \beta \frac{e^{-ikz_0}}{R_0^3} \left(C_0 - C_1 \frac{\partial}{\partial k_2 z} \right) \left\{ \frac{32\pi}{3} R_0^3 + \frac{\iota}{k_2} \right. \end{aligned}$$

$$\begin{aligned}
& \times \int_0^{2R_0} \int_0^\pi \int_0^{2\pi} \frac{1}{r} [1 - ikR \cos \Theta \dots] R^2 dR \sin \Theta d\Theta d\Phi \Big\} \\
& + \frac{3}{4\pi} \beta \frac{e^{-ikz_0}}{R_0^3} C_1 \frac{\partial}{\partial k_2 z} \left[\frac{ik_2}{2} \int_0^{2R_0} \int_0^\pi \int_0^{2\pi} r R^2 dR \sin \Theta d\Theta d\Phi \right. \\
& \left. + \frac{k^2}{2k_2} \int_0^{2R_0} \int_0^\pi \int_0^{2\pi} \frac{R^2}{r} \cos^2 \Theta R^2 dR \sin \Theta d\Theta d\Phi \right] \\
& = \frac{3}{4\pi} \beta \frac{e^{-ikz_0}}{R_0^3} \left(C_0 - C_1 \frac{\partial}{\partial k_2 z} \right) \left[\frac{3}{2} \frac{2\pi}{R_0^3} + \frac{1}{k_2} \right. \\
& \times \int_0^{2R_0} \int_0^\pi \int_0^{2\pi} \frac{1}{r} [1 - ikR \cos \Theta \dots] R^2 dR \sin \Theta d\Theta d\Phi \Big] \\
& + \frac{3}{4\pi} \beta \frac{e^{-ikz_0}}{R_0^3} \frac{1}{2} C_1 \\
& \times \int_0^{2R_0} \int_0^\pi \int_0^{2\pi} \frac{2\pi z - z_0 - R \cos \Theta}{r} R^2 dR \sin \Theta d\Theta d\Phi \\
& + \frac{3}{4\pi} \beta \frac{e^{-ikz_0}}{R_0^3} \frac{C_1}{2} \frac{k^2}{k_2^2} \\
& \times \frac{\partial}{\partial z} \int_0^{2R_0} \int_0^\pi \int_0^{2\pi} \frac{1}{r} R^2 \cos^2 \Theta R^2 dR \sin \Theta d\Theta d\Phi. \quad (45)
\end{aligned}$$

In the evaluation of this integral we find integrals of the form

$$\int_0^{2R_0} \int_0^\pi \int_0^{2\pi} \frac{1}{r} R^n \cos^n \Theta R^2 dR \sin \Theta d\Theta d\Phi.$$

We remark that they represent the electrostatical potential at a point xyz inside of a sphere of radius $2R_0$, in which there is a positive electric density distributed according to $R^n \cos^n \Theta$. We therefore solve the Laplace equation

$$\Delta V = -4\pi R^n \cos^n \Theta$$

with the conditions of continuity of V and $\frac{\partial V}{\partial R}$ on the surface

of the sphere and a vanishing potential at infinity. We get

$$\begin{aligned} \int_0^{2R_0} \int_0^\pi \int_0^{2\pi} \frac{1}{r} R^2 dR \sin \Theta d\Theta d\Phi &= \frac{4\pi}{6} (12R_0^2 - R^2), \\ \int_0^{2R_0} \int_0^\pi \int_0^{2\pi} \frac{1}{r} R \cos \Theta R^2 dR \sin \Theta d\Theta d\Phi &= \frac{4\pi}{10} R \cos \Theta (6R_0^2 - R^2), \\ \int_0^{2R_0} \int_0^\pi \int_0^{2\pi} \frac{1}{r} R^2 \cos^2 \Theta R^2 dR \sin \Theta d\Theta d\Phi &= \frac{4\pi}{3} \left(4R_0^4 - \frac{R^4}{20} \right) + \frac{4\pi}{3} R^2 \left(\frac{4}{15} R_0^2 - \frac{R^2}{7} \right) P_2(\cos \Theta) \\ &= 4\pi \left[\frac{R^4}{140} - \frac{1}{14} R^2 z^2 + \frac{2}{5} R_0^2 z^2 - \frac{2}{15} R_0^2 R^2 + \frac{4}{3} R_0^4 \right]. \end{aligned} \quad (46)$$

This leads then to the following potential (45) of the "Lorentz-Lorenz force":—

$$\begin{aligned} \psi_e'' &= \frac{3}{4\pi} \frac{\beta}{R_0^3} e^{-\iota k z_0} \left(C_0 - C_1 \frac{\partial}{\partial k_2 z} \right) \left\{ \frac{32\pi}{3} R_0^3 \right. \\ &\quad \left. + \frac{\iota}{k_2} \left[\frac{4\pi}{6} (12R_0^2 - R^2) - \iota k \frac{4\pi}{10} R \cos \Theta (6R_0^2 - R^2) \right] \right\} \\ &\quad + \frac{3}{4\pi} \frac{\beta}{R_0^3} e^{-\iota k z_0} \frac{\iota}{2} C_1 \left[\frac{4\pi}{6} R \cos \Theta (12R_0^2 - R^2) \right. \\ &\quad \left. - \frac{4\pi}{10} R \cos \Theta (6R_0^2 - R^2) \right] + \frac{3}{4\pi} \frac{\beta}{R_0^3} e^{-\iota k z_0} \frac{C_1}{2} 4\pi \frac{k^2}{k_2^2} \\ &\quad \times \frac{\partial}{\partial z} \left[\frac{R^4}{140} - \frac{1}{14} R^2 z^2 + \frac{2}{5} R_0^2 z^2 - \frac{2}{15} R_0^2 R^2 + \frac{4}{3} R_0^4 \right] \\ &= \beta e^{-\iota k z_0} C_0 \left[\frac{\iota}{k_2 R_0} \left(6 - 8\iota k_2 R_0 - \frac{R^2}{2R_0^2} \right) \right. \\ &\quad \left. + \frac{3}{10} \frac{k}{k_2} \left(6 \frac{R}{R_0} - \frac{R^3}{R_0^3} \right) P_1(\cos \Theta) \right] \\ &\quad + \beta e^{-\iota k z_0} C_1 \left\{ \frac{k}{k_2} \frac{1}{k_2 R_0} \left(2R_0^2 - \frac{9}{5} \right) + \iota \left[\frac{1}{k_2^2 R_0^2} \frac{R}{R_0} \right] \right\} \end{aligned}$$

$$\begin{aligned}
 & + \frac{R}{R_0} \left(\frac{21}{10} + \frac{4}{5} \frac{k^2}{k_2^2} - \frac{1}{10} \left(1 + 3 \frac{k^2}{k_2^2} \right) \frac{R^2}{R_0^2} \right) \left] P_1(\cos \Theta) \right. \\
 & \left. + \frac{2}{5} \frac{k}{k_2} \frac{1}{k_2 R_0} \frac{R^2}{R_0^2} P_2(\cos \Theta) - \frac{3}{35} \frac{k^2}{k_2^2} \frac{R^3}{R_0^3} P_3(\cos \Theta) \right\}.
 \end{aligned}
 \tag{47}$$

In this formula the development has been extended just to the necessary limit.

The Surface Conditions.

The surface conditions are exactly the same as in the preceding paper, with the one exception that the normal tension due to the exciting field has to be written

$$\begin{aligned}
 p_{rr} = & -2\pi\nu\rho_2 \left[\frac{k^2}{k_2^2} \psi_e' + \frac{2}{k_1^2} \left(\frac{2}{r} \frac{\partial \psi_e'}{\partial r} + \frac{1}{r^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \psi_e'}{\partial \theta} \right) \right. \\
 & + \frac{1}{k_2^2 r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi_e''}{\partial r} \right) - \frac{4}{k_4^2 r} \frac{\partial \psi_e''}{\partial r} \\
 & \left. + \left(\frac{1}{k_2^2} - \frac{2}{k_4^2} \right) \frac{1}{r^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \psi_e''}{\partial \theta} \right]
 \end{aligned}$$

instead of (23), because ψ_e' satisfies the equation $\Delta\psi + k^2\psi = 0$ and not $\Delta\psi + k_2^2\psi = 0$. We then find for the member not depending on the angle Θ

$$\begin{aligned}
 \frac{\rho_1}{\rho_2} A_0 \left(1 - \frac{4k_1^2}{3k_2^2} \right) = & \iota \frac{C_0}{k_2 R_0} \left(1 - \iota k_2 R_0 - \frac{4}{k_4^2 R_0^2} \right) \\
 & + \frac{3\beta}{k_2^3 R_0^3} \frac{k_2^2}{k^2 - k_2^2} \left(C_0 \iota - C_1 \frac{k}{k_2} \right) \left(\frac{k^2}{k_2^2} - 3 \frac{k^2}{k_4^2} \right) \\
 & + \frac{1}{k_2^2 R_0^2} \left(-\frac{3\iota\beta C_0}{k_2 R_0} + 3\beta C_1 \frac{k}{k_2} \frac{1}{k_2 R_0} \right) \\
 & - \frac{4}{k_1^2 R_0^2} \left(-\frac{\iota\beta C_0}{k_2 R_0} + \beta C_1 \frac{k}{k_2} \frac{1}{k_2 R_0} \right), \tag{48}
 \end{aligned}$$

$$\begin{aligned}
 -k_1 A_0 \frac{k_1 R_0}{3} = & -k_2 \frac{\iota C_0}{k_2^2 R_0^2} - \frac{3\beta}{k_2^3 R_0^3} \frac{k_2^2}{k^2 - k_2^2} \left(C_0 \iota - C_1 \frac{k}{k_2} \right) \frac{k^2 R_0}{3} \\
 & + \frac{\iota\beta C_0}{k_2 R_0^2} - \beta C_1 \frac{k}{k_2} \frac{1}{k_2 R_0^2}, \tag{49}
 \end{aligned}$$

Subtracting from this (25'''), we find

$$\begin{aligned} \frac{\rho_1}{\rho_2} \left(\frac{k_1}{k_2} \frac{A_1}{3\epsilon} - \frac{k_3}{k_2} \frac{2B_1}{3\epsilon} \right) k_2^3 R_0^3 \\ = 3C_1 \left(1 - \frac{\beta}{3} \right) - 3\beta \frac{k}{k_2} \left(\frac{k^2}{k^2 - k_2^2} - 1 \right) \left(C_0 \epsilon - C_1 \frac{k}{k_2} \right), \end{aligned}$$

which, compared with the lowest order in (54),

$$\begin{aligned} \left(\frac{k_1}{k_2} \frac{A_1}{3\epsilon} - \frac{k_3}{k_2} \frac{2B_1}{3\epsilon} \right) k_2^3 R_0^3 \\ = -\beta C_1 - 3\beta \frac{k}{k_2} \frac{k_2^2}{k^2 - k_2^2} \left(C_0 \epsilon - C_1 \frac{k}{k_2} \right), \end{aligned}$$

gives the final result

$$C_1 = \frac{\beta}{1 - \frac{\beta}{3} \frac{\rho_2 - \rho_1}{\rho_2}} \left(C_0 \epsilon - C_1 \frac{k}{k_2} \right) \frac{k}{k_2} \left[\frac{k^2}{k^2 - k_2^2} - 1 - \frac{\rho_1}{\rho_2} \frac{k_2^2}{k^2 - k_2^2} \right] \quad . \quad . \quad . \quad (56)$$

or

$$\begin{aligned} \frac{k}{k_2} C_1 &= \frac{\beta}{1 - \frac{\beta}{3} \frac{\rho_2 - \rho_1}{\rho_2}} \left(C_0 \epsilon - C_1 \frac{k}{k_2} \right) \frac{k^2}{k_2^2} \frac{k_2^2}{k^2 - k_2^2} \left(1 - \frac{\rho_1}{\rho_2} \right) \\ &= \frac{\beta}{1 - \frac{\beta}{3} \frac{\rho_2 - \rho_1}{\rho_2}} \left(C_0 \epsilon - C_1 \frac{k}{k_2} \right) \left(\frac{k^2}{k^2 - k_2^2} \right) \frac{\rho_2 - \rho_1}{\rho_2}. \quad . \quad . \quad (56') \end{aligned}$$

Subtracting this from (50), we have on the left side also $\left(C_0 \epsilon - C_1 \frac{k}{k_2} \right)$, which can be cancelled out on both sides, leaving the expression for k^2 as a condition for the solubility of the surface conditions

$$\begin{aligned} 1 &= \beta \frac{k_2^2}{k^2 - k_2^2} \left\{ \frac{\rho_2 k_1^2}{\rho_1 k_2^2} \frac{1 - \frac{4}{3} \frac{k_3^2}{k_4^2}}{1 - \frac{4}{3} \frac{k_1^2}{k_3^2}} - 1 \right\} \\ &\quad - \frac{\beta}{1 - \frac{\beta}{3} \frac{\rho_2 - \rho_1}{\rho_2}} \frac{\rho_2 - \rho_1}{\rho_2} \left(\frac{k_2^2}{k^2 - k_2^2} + 1 \right). \quad . \quad . \quad (57) \end{aligned}$$

We solve this equation for

$$\frac{k^2 - k_2^2}{k_2^2} = \frac{V_2^2 - V^2}{V^2},$$

where V_2 is, as before, the velocity of propagation in the pure liquid, and V the velocity in the suspension. We get

$$\frac{V_2^2 - V^2}{V^2} = \frac{\beta}{1 - \frac{2}{3}\beta\frac{\rho_1 - \rho_2}{\rho_2}} \left\{ \left(1 + \frac{\beta}{3}\frac{\rho_1 - \rho_2}{\rho_2} \right) \times \left[\frac{\rho_2}{\rho_1} \frac{k_1^2}{k_2^2} \frac{1 - \frac{4}{3}\frac{k_2^2}{k_4^2}}{1 - \frac{4}{3}\frac{k_1^2}{k_3^2}} - 1 \right] + \frac{\rho_1 - \rho_2}{\rho_2} \right\}, \quad (58)$$

or, taking into account the transformations which led to (38'),

$$\frac{V_2^2 - V^2}{V^2} = \frac{\beta}{1 - \frac{2}{3}\beta\frac{\rho_1 - \rho_2}{\rho_2}} \times \left\{ \left(1 + \frac{\beta}{3}\frac{\rho_1 - \rho_2}{\rho_2} \right) \frac{K_1 - K_2}{K_2} + \frac{\rho_1 - \rho_2}{\rho_2} \right\}. \quad (58')$$

Comparing this with (38'), we see that (58') is identical with (38') if we keep only the lowest power of β and take into account the fact mentioned on p. 755 that $\frac{V_2 - V}{V}$ is approximately $\frac{1}{2} \frac{V_2^2 - V^2}{V^2}$ for small values of $V_2 - V$. It is curious

to note that for an equal density of sphere and liquid the only effect of taking into account the interaction of the particles is the replacement of $\frac{V_2 - V}{V}$ by $\frac{V_2^2 - V^2}{2V^2}$, being due to the reflected wave from particles farther ahead (p. 755).

On the other hand, if the compressibilities are equal, (58') can be put into a form which is somewhat similar to the statement in optics that the refractivity $\frac{n^2 - 1}{n^2 + 2}$ is proportional to the density, namely into the form

$$1 - \frac{V^2}{V_2^2} = \frac{\beta}{3} \frac{\rho_1 - \rho_2}{\rho_2}.$$

This similarity is probably due to the fact that the optical wave as well as the acoustical waves due to density differences can be derived from dipole sources.

If we transform equation (58') to give an evaluation of the compressibility, we find

$$\frac{K_1 - K_2}{K_2} = \frac{V_2^2 - V^2}{\beta V^2} - \frac{V_2^2}{V^2} \frac{\frac{\rho_1 - \rho_2}{\rho_2}}{1 - \frac{2}{3} \beta \frac{\rho_1 - \rho_2}{\rho_2}} \quad (59)$$

To sum up the accuracy, we have neglected $\left(\frac{2\pi R_0}{\text{wave-lengths}}\right)^2$ compared with unity. By this restriction we have accomplished that only β , which represents the fraction of the volume filled by the suspended particles, appears. It may be hoped, therefore, that our result will also be valid if the form of the particles deviates from spheres. Furthermore, if the particles are not isotropic, it seems probable that, due to the random orientation, they will act like particles of an isotropic solid with constants calculated according to Voigt*, who gave formulæ for the behaviour of a microcrystalline substance built from anisotropic grains of random orientation.

We have neglected the damping of the longitudinal waves in the liquid, and the contribution of the transversal waves to the exciting field, which is justified for water if the frequency is sufficiently high; but otherwise we have not made any assumption about the smallness of β (the amount of suspended material). Finally, we have neglected in the equations of motion of the viscous fluid squares of the velocities, which means we have assumed that the intensity is small, and we have simply spoken of compressibility without specifying the difference between isothermal and adiabatic compressibility. In a uniform medium the latter should be taken, but here we might have heat conduction from the liquid to the solid, and as the difference between the two compressibilities is small, this will not make any difference.

Conclusion.

Formulas for the velocity of sound in a suspension of small solid particles have been developed. These can be used to calculate the compressibility of the solid materials from measurements of the velocity of propagation. Such experiments have been started in this laboratory.

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* W. Voigt, *Gott. Abh.* xl. (1887); *Wied. Ann. d. Phys.* xxxviii. pp. 573 (1889).

LXXI. *Investigation of the Cataphoresis of small Particles in Water.* By DOROTHY A. NEWTON, B.Sc.*

INTRODUCTION.

IN 1808, Reuss ⁽¹⁾ observed the fact that when a porous diaphragm separates two parts of a liquid through which an electric current is flowing, the liquid flows through the membrane sometimes towards the anode, but more often towards the cathode. This phenomenon was termed electric endosmosis. In 1861, Quinke ⁽²⁾ observed the fact that air bubbles in water through which an electric current was passing moved towards the anode, acting as if negatively charged. The same effect has since been observed for liquids and solid drops in water. This motion is termed cataphoresis.

Helmholtz ⁽³⁾ was the first to attempt to give a theoretical explanation of endosmosis and cataphoresis. He showed that both could be explained, if it was assumed that there existed an electrical double layer at the boundary of the two substances. In the case of endosmosis, it is assumed that the layer next to the diaphragm is fixed to the surface, but the layer within the liquid is free to move, so that when a P.D. is maintained between the liquid on the two sides of the diaphragm, the mobile part of the double layer moves through the pores, dragging with it, by viscous drag, the neighbouring liquid. In the case of cataphoresis, one layer resides in the surrounding liquid and the other on the surface of the particle, causing it to act as if it were charged when placed in an electric field. The velocity acquired by such a particle was calculated by Helmholtz, and is given by

$$V = \frac{x\rho d}{\eta}$$

$$= \frac{k\sigma c}{4\pi\eta} \times \text{radial voltage in double layer,}$$

where

x = the electric field,

ρ = surface density of charge on the particle.

d = distance between two layers of electricity,

* Communicated by Prof. J. A. Crowther, M.A., Sc.D. Thesis presented for the Degree of M.Sc. in the University of Reading.

η = coefficient of viscosity of the liquid,

k = specific inductive capacity,

σ = specific resistance of liquid,

c = current per unit area.

According to this formula, V is directly proportional to the applied electric field. This has been verified experimentally for air bubbles in water by McTaggart ⁽⁴⁾ and for oil drops in water by Mooney ⁽⁵⁾. Also, the velocity of the drop should be independent of its size. Alty ⁽⁷⁾ has shown that this is not true for bubbles of air in water. He finds that for large air bubbles of diameter 2 mm. the velocity is small and the bubbles move as if negatively electrified. This velocity steadily increases as the diameter decreases, until the latter is reduced to about .25 mm., near which size the velocity attains a maximum and remains fairly constant until the diameter is about .15 mm. For diameters less than this the velocity decreases steadily until the bubble disappears. Mooney found that for oil drops ranging in diameter from $.05 \times 10^{-3}$ cm. to 4×10^{-3} cm., in a field of 10 volts per cm. the velocity gradually decreases with the diameter. Hardy ⁽⁶⁾, employing the U-tube method and working with a colloidal solution of globulin, found that his results were in agreement with Helmholtz's theory over a wide range of diameters, but he states that when the diameters were so large as to give a milky coloration, the velocity falls off as the size increases.

It thus appears that the theory holds for small colloidal particles, but is not adequate for microscopic particles.

When observations are made on drops or bubbles in water in a closed cell, the observed velocity neglecting gravity, when an electric field is applied, is due to the cataphoretic velocity of the bubble together with the endosmotic velocity of the water. On Helmholtz's theory the mobile part of the double layer at the walls of the cell moves when an electric field is applied, and as the cell is closed there must be a return flow along the axis of the tube. In a later part of the paper it is shown how the true cataphoretic velocity of a bubble may be determined. Both McTaggart and Alty have assumed in their work that the effect of endosmosis may be neglected except at a small distance from the wall of the cell, and have made

observations on bubbles on the axis of the cell and termed the observed velocity the cataphoretic velocity of the bubble. That their assumption is not correct is shown by results given later in this paper. To obtain the true value of the cataphoretic velocity, it would be necessary to

Fig. 1.



subtract from their value the endosmotic velocity of the water on the axis of their tube.

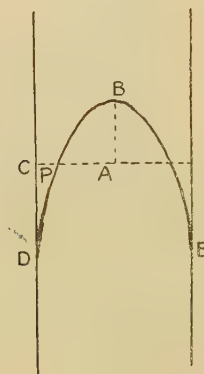
Apparatus.

In the present investigation experiments were chiefly done on oil drops in water. The form of cell used is shown in fig. 1. It consists of a glass tube 20 cm. in length

of internal diameter 0.7 cm. with a small piece of platinum carrying a platinum wire fused into one end to form the lower electrode. The upper electrode consists of a piece of platinum bearing a platinum wire passing through a rubber cork which fits closely into the upper end of the tube. To avoid distortion of the optical image of a bubble in the cell due to the curvature of the glass tube, a small hole (about 1 mm. in diameter) was bored in the tube at the centre, the glass ground flat at this place, and a small piece of cover-slip cemented on to the tube to act as a window.

The cell was cemented into a brass tube about 18 cm. long, 1 cm. in diameter, fitted with two glass windows

Fig. 2.



diametrically opposite in the centre of the tube. The cell was so placed that its small cover-slip window was opposite one of the windows of the brass tube, as shown in fig. 1. The space between the tube and the glass cell was filled with water to maintain a uniform temperature throughout the cell. The brass tube was supported in a cubical box, pierced with two holes, one in each of two opposite vertical sides. The tube was so placed that its windows faced these holes, so that light from a lamp passed through one to illuminate a bubble inside the cell, and the object-glass of a horizontal microscope placed in the other allowed the bubble to be viewed. A water cell interposed between the cell and the lamp absorbed the heat rays.

All experiments were made in a dark room, the temperature throughout being about 15° C.

To apply an electric field across the cell, the electrodes were connected through a reversing key and two resistance lamps to the 210-volt mains.

Distances perpendicular to the axis of the microscope were measured by means of a scale in the eyepiece. Each division of the eyepiece scale corresponds to 2.4×10^{-3} cm. Distances parallel to the axis of the microscope were measured by means of a graduated horizontal scale on the microscope. Time measurements were made with a stop watch which could be read to $\frac{1}{10}$ sec.

Theory.

As has been stated in an earlier part of the paper, the observed velocity of a bubble or drop due to the electric field in liquid in such a cell as described above, neglecting effect of gravity, is composed of the true cataphoretic velocity of the drop together with the endosmotic velocity of the water in the neighbourhood of the drop. The water near the wall of the cell has a velocity parallel to the axis, due to the effect of endosmosis. As the cell is a closed one this causes a return flow in the central portion of the cell. At one point along the radius of the cell the water must be stationary, since the water at the axis of the cell is flowing in one direction and in the opposite direction at the wall. It can be shown that in these circumstances the velocity distribution across the cell will be parabolic, except near the ends of the cell.

In fig. 3 let DPBE represent the velocity distribution across the cell.

Let $CD = v_w$, the velocity of the water at the walls,

$AB=v_c$, the velocity of the water at the centre,

P be a point on the stationary layer,

$$AP = p,$$

r = radius of tube.

Then, since the cell is closed and P the stationary layer, the volume DCP = volume PBA.

$$\text{Volume DCP} = \pi r^2 v_w - \frac{1}{2} \{ \pi r^2 (v_w + v_c) - \pi p^2 v_c \}.$$

$$\text{Volume PBA} = \frac{1}{2} \pi p^2 v_c.$$

[illegible]

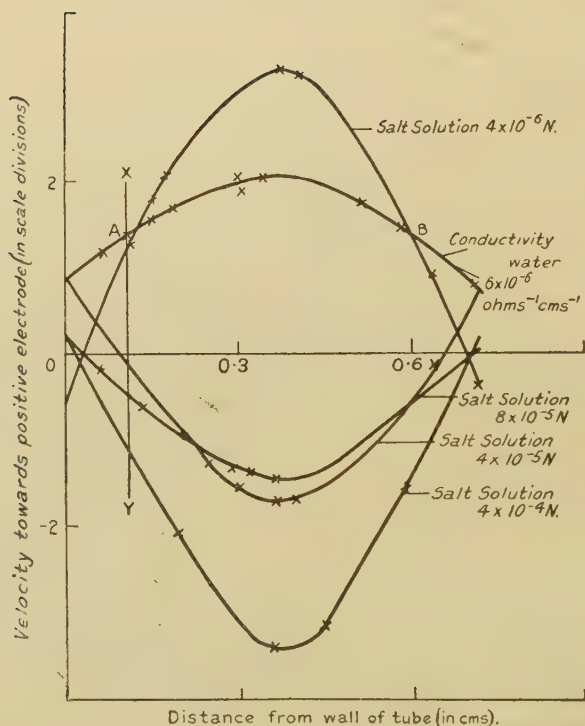
Also, since the curve is parabolic,

$$\frac{p^2}{r^2} = \frac{v_c}{r_x v_c}$$

$$= \frac{1}{2}, \text{ using equation (i.)}$$

$$p = \frac{r}{\sqrt{2}}.$$

Fig. 3.



Thus the stationary layer is at a distance $\frac{r}{\sqrt{2}}$ from the axis.

The fact that the distribution of velocity across the tube is parabolic is shown to be experimentally correct by velocity curves given in this paper.

The observed velocity, therefore, of a drop at a distance $\frac{r}{\sqrt{2}}$ from the axis, where r is the radius of the cell, would

be its true cataphoretic velocity, since the endosmotic velocity of the water at this point is nil.

This fact was used in the present investigation to find the true cataphoretic velocity of oil drops in water.

*Experimental Determination of Cataphoretic Velocity
of Oil Drops in Water.*

A mixture of distilled water and a few drops of paraffin oil (density $\cdot 82$, viscosity $\cdot 033$) was well shaken in a separating funnel and allowed to stand until the larger drops of oil had risen. The fine emulsion of oil drops in water at the bottom of the vessel was allowed to run into the glass cell, the rubber stopper carrying the upper electrode was placed in position, and the cell put into the wooden box in an upright position with its cover-slip window facing the microscope. The apparatus was left for a short while to come to a steady temperature.

The microscope was moved by means of a screw until the front wall of the cell was in focus. The reading of the horizontal scale was noted. The microscope was then moved forward until a drop of a suitable diameter was sighted in the centre of the scale. Its velocity was timed with the electric field first in one direction and then in the other and the reading of the horizontal scale of the microscope noted. This was done for a number of drops across the tube. As Mooney ⁽⁵⁾ has shown that for oil drops in water the velocity is not independent of the size of the drop, throughout the experiments observations have been made only on drops of diameter equal to 1 division on the eyepiece scale, which equals $2\cdot 4 \times 10^{-3}$ cm.

The observed velocity of the drop is due to the sum of the effects of gravity and the electric field. To find the effect of the electric field, let

V_F = velocity due to field,

V_g = velocity due to gravity,

V_U = observed velocity of bubble when field is in one direction,

V_p = observed velocity of bubble when field is in other direction (all measured in the same sense).

Then

$$V_F = \frac{V_U - V_p}{2} \quad \dots \quad \text{(ii.)}$$

The velocity of the bubble due to the field was obtained by (ii.) from observations of V_v and V_p . By this method the effect of slow convection currents which may occur in the liquid is eliminated.

A curve was then plotted between V_F and the distance of the drop from the front inner wall of the tube. The true cataphoretic velocity of the drops of diameter equal to 2.4×10^{-3} cm. may be read off from the curve—it is the velocity of a drop at the stationary layer, *i. e.* at a distance $\frac{r}{\sqrt{2}} = \frac{.35}{\sqrt{2}}$ cm. from the centre of the tube. A

typical curve obtained for oil drops in water of conductivity 6×10^{-6} ohm $^{-1}$ cm. $^{-1}$ is AB in fig 3. The cataphoretic velocity of a bubble is given by the value at A or B on the curve—the mean of these two readings is taken as the correct value. For the curve AB of fig. 3 it is seen to be 3.17×10^{-3} cm./sec. The field across the tube is 10 volts/cm. The cataphoretic velocity of drops in water of conductivity 6×10^{-6} ohm $^{-1}$ cm. $^{-1}$ may therefore be expressed as 3.17×10^{-4} cm./sec./volt/cm.

It will be seen from fig. 3 that curve AB is symmetrical about the axis, thus showing that the small cover-slip window has a negligible effect on the flow of water at a small distance from the walls.

Every curve obtained was of the parabolic form of the curve represented in fig. 3, as is required by the theory of the cell given above. If, as McTaggart and Alty assumed, the effect of endosmosis may be neglected at a short distance from the walls, the observed velocity of bubbles of the same diameter at all positions across the tube, except near the walls, should be the same. This is obviously not the case, as may be seen from any of the velocity curves given in this paper. It must therefore be concluded that the assumption of McTaggart and Alty is incorrect, and that from their values of the observed velocity of the drops must be subtracted a constant depending on experimental conditions, to obtain the cataphoretic velocity of the bubbles.

If V_F = the velocity of a drop at the stationary layer,

V_C = the observed velocity of a drop at the centre of the tube,

V_W = the observed velocity of a drop at the wall of the tube (all measured in the same sense).

then, from the theory of the cell,

$$V_C - V_F = V_F - V_W.$$

It was found on examination of the curves that this was true within the limits of experimental error.

The value $V_C - V_F$ = endosmotic velocity of the water at the wall of the cell for the particular experiment. Hence the endosmotic velocity of the water under observation may be found from the velocity curve. An attempt was made to obtain very small beads of the same glass as the wall of the tube to see if the endosmotic velocity in that case was equal and opposite to the cataphoretic velocity, as deduced from Helmholtz's theory. The velocity under gravity of the smallest obtainable, however, was too great for any observations to be taken, so the comparison could not be made.

*Effect of introducing small Traces of $Th(NO_3)_4$
into the Water.*

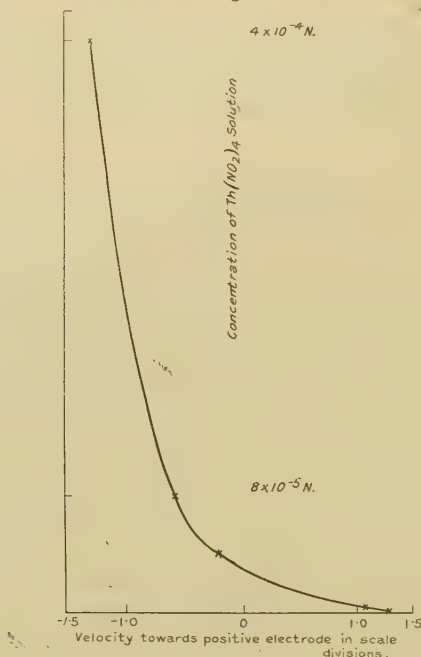
Mooney made one or two observations on oil drops in very dilute salt solution, but no very definite results were obtained. It was therefore thought worth while to investigate further to see whether the addition of salt had the same effect on oil drops as McTaggart found it to have on air bubbles, *i. e.* of decreasing the charge to zero and ultimately reversing it.

The conductivity of the water used in the present experiments was of the order of 6×10^{-6} ohm $^{-1}$ cm. $^{-1}$. A standard solution of 4×10^{-4} Normal was made up, and from it solutions of concentration 4×10^{-4} N., 8×10^{-5} N., 4×10^{-5} N., and 4×10^{-6} N. were obtained. Observations were made on the velocity of oil drops in each of the four solutions and in pure water, and velocity curves plotted as described above. A solution of salt greater than 4×10^{-4} N. causes the conductivity of the liquid to become so great that bubbles of gas are evolved at the electrodes almost immediately the field is applied, and consequently no observations could be made. The curves obtained for these solutions are given in fig. 3. The line XY represents the position of the stationary layer, and the velocity at that point is the cataphoretic velocity of the bubbles observed. Fig. 4 shows the relationship between the cataphoretic velocity and the concentration of salt. It will be seen from this curve that the drop behaves as an

uncharged particle when the salt concentration is 3×10^{-5} N.

Although the cataphoretic velocity towards the positive electrode decreases steadily until for 4×10^{-4} N. it has a negative value, the endosmotic velocity as given by the difference between the observed velocity at the centre of the tube and the stationary layer is a little irregular. This is possibly owing to the fact that the curves were not obtained in order, and thus all traces of the salt may not

Fig. 4.



have been removed from the walls after each experiment, but it is interesting to note that the addition of salt ultimately changes the direction of movement at the walls, *i. e.* the sign of the charge of the mobile part of the double layer, in the same way as the sign of the charge on the bubble is ultimately reversed.

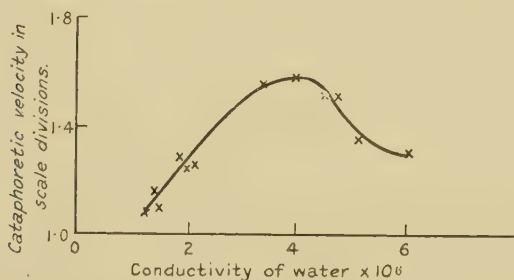
No satisfactory explanation has yet been put forward of the effect that small traces of salt have on the cataphoretic velocity of the drops or bubbles. The phenomenon has been found to be true for colloidal solutions, air

bubbles, and, by this present work, for oil drops in water. It is thought that in some manner the ions of the salt "cover" the ions in the double layer and so neutralize the effective charge on the drop.

Effect of the Conductivity of the Water.

The conductivity of the water used in the previous experiments was about $6 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$. To obtain purer water than this a still similar to the one described in a paper by Bourdillon in the 'Journal of the Chemical Society,' 1913, was used. The water was collected in a hard glass flask fitted with a rubber cork into which a soda-lime tube was fitted and a siphon tube, so that the water could easily be run out without removing the rubber

Fig. 5.



stopper. Observations were made on oil drops in this purer water, and the cataphoretic velocity of the drops obtained from the velocity curves as described above. Experiments were carried out with water of conductivity ranging from 1.3×10^{-6} up to about $8 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$. A curve was drawn connecting the cataphoretic velocity with the conductivity of the water, and is given in fig. 5. It will be seen that there is a definite maximum cataphoretic velocity at a conductivity of $4 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$, and that the velocity decreases more rapidly at first on the higher conductivity side, but at about 6×10^{-6} becomes more or less constant at velocity of $3.17 \times 10^{-3} \text{ cm./sec.}$ On the lower conductivity side the velocity drops quite rapidly until at a conductivity of $1.3 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$ it is $2.5 \times 10^{-3} \text{ cm./sec.}$ under $\frac{2}{3}$ of its value at $4 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$.

Alty⁽⁷⁾ describes some experiments on air bubbles in water of different conductivities. He found that the bubbles had a smaller velocity in pure water, conductivity about $2 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$ than in distilled water of higher conductivity, that the velocity rose to a maximum and fell off fairly quickly at first on the higher conductivity side. The value he gives of the conductivity water at maximum velocity, $8 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$, is decidedly higher than the one obtained in the present experiments. The two results, however, cannot easily be compared, as the smallest air bubble used was 1 mm. in diameter and the cataphoretic velocity of a drop is not independent of its diameter. It does, however, seem to be quite evident in both experiments that the velocity rises to a definite maximum as the conductivity of the water is varied.

It was hoped when this set of experiments were commenced to obtain very pure water of conductivity about $0.5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$. Bourdillon claims in his paper that, from the form of still described, water of conductivity as low as $1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$ could be obtained. Since Reading water is contaminated with chlorine, the boiler was filled with filtered rain-water. When, however, the conductivity of the water produced was introduced into the glass vessel and measured by a reflecting moving coil galvanometer, in no case was it less than $1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$. It was therefore not possible to discover whether the drop in very pure water ultimately had no charge.

Hardy⁽⁶⁾, working with colloidal solutions of globulin, found that the velocity was very much reduced in pure water, so that the results obtained in these experiments on oil drops in pure water agree with those obtained with air bubbles and some colloidal solutions.

Effect of adding Alcohol to Water.

To determine whether the addition of alcohol to the water affects the cataphoretic velocity of the drops, some experiments were made on oil drops in different mixtures of water and absolute alcohol. The conductivity of the water used was about $5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$. Observations were made on oil drops in mixtures of 10 per cent., 20 per cent., 100 per cent. alcohol, and the cataphoretic velocity of the drop obtained from the curves in the usual manner. A curve was then drawn connecting the cata-

phoretic velocity with the percentage of water in the liquid, and is given in fig. 6. It will be seen that the velocity steadily decreases as the percentage of water decreases, until, when the percentage of water equals about 48, the velocity is reduced to zero and remains zero for further reduction in the proportion of water. Velocity curves show that the endosmotic velocity of the water is also reduced in the same manner.

Fig. 6.

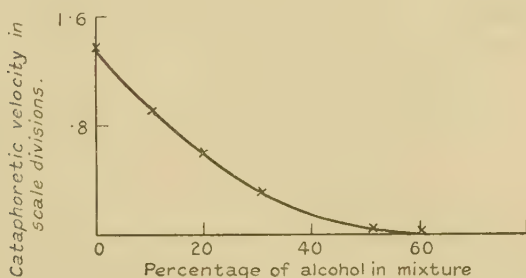
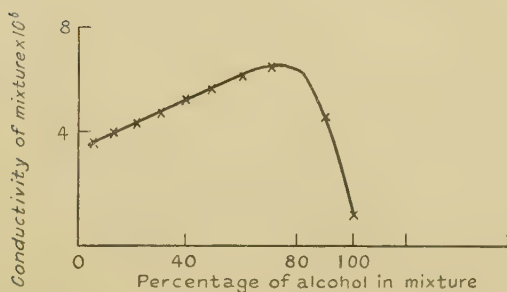


Fig. 7.



To find if the conductivity of the mixture had any bearing on this effect, the conductivity for different mixtures as measured by the moving-coil galvanometer was plotted against the percentage of water, and the result is given in fig. 7. On comparing the two curves, fig. 6 and fig. 7, there does not appear to be any obvious connexion between the conductivity and the cataphoretic velocity; in fact, the conductivity is just rising to a maximum when the cataphoretic velocity falls to zero.

By the theory developed by Helmholtz, embodied in the equation quoted in the first part of this paper, there

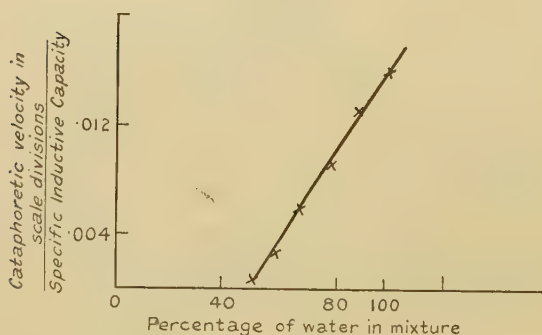
should be some relationship between the specific inductive capacity of the liquid and the cataphoretic velocity of a drop in the liquid. To test this the values of the specific inductive capacity of different mixtures of alcohol and water were obtained from the 'International Critical Tables,' and a curve drawn relating to ratio

$$\frac{\text{cataphoretic velocity of the drop}}{\text{specific inductive capacity}}$$

to the percentage of water in the mixture. The result is given in fig. 8. From this curve the relationship is seen to be linear, and may be represented by

$$\frac{V}{K} = ax - b,$$

Fig. 8.



where a and b are constants.

V = cataphoretic velocity of the bubble,

K = specific inductive capacity of the mixture,

x = percentage of water in the mixture.

It is difficult to see just how the introduction of the alcohol into the water reduces the charge on the double layer to zero. As in the case of very pure water, we have the fact of the velocity being reduced to zero when there are still numbers of ions in the liquid. There is no indication of any reversal of the sign for further decrease in the percentage of water. The velocity remains nil, so that the effect does not appear to be similar to that

found when small traces of salt are introduced into the water, which was accounted for by supposing that the ions in the double layer were "covered" by ions of the opposite sign, and thus the charge is reduced to zero and ultimately reversed.

Effect of other Substances in Water.

Some very interesting results were obtained when experiments were made on substances in water other than paraffin oil. The following is a list of different substances on which observations were made :—

Bakelite.	Oil of cloves.
Aluminium.	Oil of lavender.
Barium carbonate.	Soft wax.
Copper.	Beeswax.
Starch.	Calspar.
Zinc oxide.	Resin.
Titanic acid.	

Where possible the substance was broken up under water to avoid the possibility of there being an air film around the small particles. In no case was it found that the cataphoretic velocity was towards the negative electrode—all substances acted as if negatively charged. It appears from this set of experiments that for microscopic particles, at least, all suspensions in water act as if negatively charged. This is contrary to some results quoted in chapter vii. of Burton's book on 'Physical Properties of Colloidal Solutions.' This is probably due to the fact that in former experiments on cataphoresis the effect of endosmosis does not seem to have been considered.

It was noticed, on inspecting the results, that the cataphoretic velocity obtained for broken bits of substances was always very much less than that outlined for spheres. An attempt was therefore made to make observations on the same substance in spherical and in broken form. It was obviously not possible to do this with many substances, since the diameter of the spheres to be experimented on should be of the order of 2.4×10^{-3} cm. To obtain spheres of this size it was necessary to experiment with a substance which melted at a temperature below 100° C., so that it could be shaken up with boiling water into very small drops and allowed to cool. It was found that by this

method very small spheres of spermaceti, stearin, naphthalene, beeswax, resin, and soft wax could be obtained. Small bits of these substances were got by filing them under water, and experiments were made on the spherical and broken form of each in water of conductivity about 4×10^{-6} ohm $^{-1}$ cm. $^{-1}$. The results are given in the following table:—

Substance.	Velocity in spherical form.	Velocity in broken form.
Spermaceti	3.78×10^{-4} cm./sec./volt/cm.	1.71×10^{-4} cm./sec./volt/cm.
Stearin ...	3.05×10^{-4} " " "	2.19×10^{-4} " " "
Naphthalene	3.78×10^{-4} " " "	2.3×10^{-4} " " "
Beeswax...	3.9×10^{-4} " " "	0 " " "
Resin	3.9×10^{-4} " " "	2.19×10^{-4} " " "
Glass		2.08×10^{-4} " " "
Soft wax...	3.9×10^{-4} cm./sec./volt/cm.	

From the above results it appears that the shape as well as the size of the particle have a bearing, in some manner, on the cataphoretic velocity, neither of which effects is allowed for in the Helmholtz theory. As may be seen, the velocity obtained for all spheres have about the same value, 3.9×10^{-4} cm./sec./volt/cm., the value obtained for oil drops in water of conductivity 4×10^{-6} ohm $^{-1}$ cm. $^{-1}$. The low result of stearin in spherical form may be accounted for by the fact that the spheres were not absolutely spherical, but tended to be rather of an elliptical shape. Except for beeswax, which apparently has no charge when in broken form, all broken particles have a velocity of about 2.2×10^{-4} cm./sec./volt/cm.

It seems from this that the fundamental factor in determining the charge of the double layer on a drop or particle is the liquid surrounding it and the size and shape of the particle. The nature of the composition of the particle appears to have little bearing on the charge. Alty⁽⁷⁾, working on bubbles of different gases, found that the observed velocity was the same irrespective of the nature of the gas. If the composition of the drop has little or no effect on the charge, it would be expected that all particles should have the same sign of charge in the same liquid, as was found with all substances on which experiments were made. It thus appears, both from Alty's results and those described here, that if the charge can be

explained by ions being adsorbed on the surface, it must be assumed that all the ions are contributed by the liquid surrounding the drop, and except for its shape and size, the nature of the drop is immaterial.

Effect of X-Rays on small Oil Drops.

A short time ago some work was done in this laboratory to investigate the effect of X-rays on colloidal particles and it was thought worth while to extend the investigations to drops visible in a low-power microscope. The method first adopted was that of trying to keep an oil drop stationary in water by means of the application of a suitable electric field ; to pass X-rays from a Shearer tube through the liquid in the neighbourhood of the drop, and by measuring its velocity before and after exposure in a field of greater strength to discover the effect, if any, of the X-rays on the drop. It was found, owing to slow convection currents in the liquid, which could not be eliminated, that it was impossible to keep the drop stationary for any length of time, and since, owing to endosmotic velocity of the water, it was only possible to compare the velocity due to cataphoresis of a bubble at different times if the drop was in the same position, it was obvious that another method would have to be employed.

The method finally adopted was that of X-raying the emulsion as a whole, and then finding the cataphoretic velocity of the drops by the method described earlier. A small, cylindrical, hard-glass dish was made to contain the emulsion to be exposed, of cross-section equal to that of the X-ray beam at a distance of about 1 cm. from the aluminium window in the X-ray tube. A little lead plate was made to hold it in position. The oil and water were shaken up as before and the glass vessel filled with the emulsion. A sample of the same emulsion was placed in another vessel to act as a standard. The X-ray tube was run for a considerable time, up to 2 hours. The current through the tube was kept at 3 milliamps., and the high potential was of the order of 60,000 volts. After the exposure the emulsion was poured into the long glass cell used in previous experiments, observations were made on drops across the tube, and the cataphoretic velocity obtained as before. The cell was then thoroughly washed out, the standard solution poured in, and the cataphoretic velocity obtained.

Although four sets of experiments, as described above, were performed on oil drops in water, the times of exposure varying from 40 minutes, up to 2 hours, in no case was there any indication of the X-rays having had any permanent effect on the drops.

In the work done on colloids in this laboratory, it was found that X-rays had no effect on any of the negatively-charged particles tried. Oil drops in water act as if they were negatively charged. If, therefore, the charge on the small microscopic drop is of the same nature as the charge on particles in a colloidal solution, the results found in these experiments would appear to substantiate those obtained earlier. As has been observed earlier in the paper, no substance could be found which was positively charged in water; thus the positive results obtained with X-rays on colloids could not be tested for oil drops. The method used here could only detect a permanent effect on the particles, and therefore it is uncertain whether or not the X-rays have a temporary effect on the drops on which experiments were made.

Summary.

The chief results of this work are summarized below :—

(i.) Small traces of $\text{Th}(\text{NO}_3)_4$ in water reduce the charge on an oil drop and eventually reverse it. Using water of conductivity $6 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$, a concentration of $3 \times 10^{-5} \text{ N.}$ reduces the charge to nil.

(ii.) The cataphoretic velocity of an oil drop rises to a maximum of $3.9 \times 10^{-4} \text{ cm./sec./volt/cm.}$ for water of conductivity $4 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$. In purer water the velocity is much less, falling to $2.5 \times 10^{-4} \text{ cm./sec./volt/cm.}$ for water of conductivity $1.3 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$.

(iii.) Addition of alcohol to the water causes the velocity to be reduced to zero when 47 per cent. of the mixture is water.

(iv.) The velocity (V) is shown to be related to the specific inductive capacity (K) for mixtures of alcohol and water by the equation $V=K(ax-b)$, where a and b are constants and x the percentage of water in the liquid.

(v.) All substances tried act as if negatively charged in water.

(vi.) Spherical drops have a much higher cataphoretic velocity than broken bits of the same substance.

(vii.) Solid and liquid spherical drops of all substances tried have a velocity of 3.9×10^{-4} cm./sec./volt/cm. in water of 4×10^{-6} ohm $^{-1}$ cm. $^{-1}$ conductivity.

(viii.) X-rays have no permanent effect on the charge of oil drops in water.

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- (8) McTaggart, *Phil. Mag.* xxviii. (1914).
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In conclusion I should like to express my thanks to Professor Crowther and Dr. Bond for the great interest they have shown and the help given in the progress of this work.

Department of Physics,
University of Reading,
Dec. 31st, 1929.

LXXII. *The Quantum Theory of X-Ray Exposures on Photographic Emulsions**. By L. SILBERSTEIN and A. P. H. TRIVELLI †.

[Plate X.]

Introduction.

IN 1922 L. Silberstein⁽¹⁾ proposed the quantum theory of light exposure on photographic emulsions, based on the assumption that every grain becomes developable with every absorbed light quantum. An analogous case is that of α -particles. Kinoshita⁽²⁾, and still more conclusively Th. Svedberg⁽³⁾, have shown that every α -particle hitting a silver halide grain of a photographic emulsion makes it developable. The sensitivity of the grain is, therefore, determined by its projective area, and the probability

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† Communicated by the Authors.

that a grain (in a one-grain layer) will be made developable by exposure to α -particles is given by the equation :

$$p = 1 - e^{-na}$$

where a = the projective area of the grain and n = the number of α -particles per unit-area of plate. The only difference from Silberstein's quantum theory in its simplest form was that the α -particle was replaced by the light dart, light being regarded as discrete in nature, and every light dart containing one quantum of energy. When using a great range of sizes of large clumps of grains the experimental investigations of A. P. H. Trivelli and F. L. Righter⁽⁴⁾ were, in the beginning, in good agreement with the results of the quantum theory.

Independently of this theory a chemical theory of sensitivity had developed, founded by J. M. Eder⁽⁵⁾ and supported by Lüppo-Cramer⁽⁶⁾, Th. Svedberg⁽⁷⁾, and F. F. Renwick⁽⁸⁾. According to this, statistical variation of sensitivity is inherent, *i. e.*, exists previously to exposure to light. It was supposed to be caused by specks or nuclei of a substance other than silver bromide. This substance was provisionally termed the photocatalyst.

In 1909 Lüppo-Cramer⁽⁶⁾ showed that chromic acid could desensitize photographic emulsions, and suggested that it was due to destruction of ripening nuclei. In a letter to the 'British Journal of Photography'⁽⁹⁾ it was suggested by S. E. Sheppard that certain specific desensitizing experiments might afford a means of distinguishing a pure quantum action from the sensitivity nucleus theory. The investigations of E. P. Wightman, A. P. H. Trivelli, and S. E. Sheppard⁽¹⁰⁾ on the distribution of sensitivity and size of grain in photographic emulsions show that the action of a desensitizer, such as chromic acid, must be due to the destruction of pre-existing specks or nuclei, which are not silver halide, confirming Lüppo-Cramer's investigations. W. Clark⁽¹¹⁾ and F. C. Toy⁽¹²⁾ confirmed the results obtained and added new evidence, so that there was no doubt of the existence of a sensitivity-promoting substance other than silver bromide distributed in specks among the grains. Strong evidence has been advanced by S. E. Sheppard⁽¹³⁾ that these sensitivity centres or sensitizing specks contain silver sulphide. In the meantime it was shown by L. A. Jones and A. L. Schoen⁽¹⁴⁾ that in the experiments of A. P. H. Trivelli and F. L. Righter,

which L. Silberstein used to test his equation, the number of quanta incident at $\lambda 470 \text{ m}\mu$ was about 4.7×10^{12} per cm^2 . This means that only a small fraction of the grain area—between 0.00001 and 0.0001—could be regarded as sensitive, if the premise is to be maintained that a grain is made developable when hit by a single light dart, absorbing one quantum. This opinion and new sets of experimental data led L. Silberstein⁽¹⁵⁾ to modify the original formula. The simplest modification consists in replacing the exponent na by $n\epsilon a$, in which ϵ =the fraction of the area of a silver halide grain which is vulnerable, *i. e.*, ready to become developable on being hit by a light dart. It was considered by L. Silberstein that the main results would not be greatly altered if the simple assumption is replaced by a more general one. According to this, let the sensitive part of the area of a grain, instead of being in a lump, consist of a number of separate vulnerable or sensitive spots, each of area ω , and distributed haphazardly among the individual grains (each of area a). The necessary and sufficient condition for a grain to be made developable will now be that at least one of its spots should be hit by at least one light dart of sufficiently short wave-length.

This theory appeared to represent, roughly at least, the observed facts. The discrepancies between the theoretical results and the experimental findings, *viz.*, the number of grains of a given size made developable by a given exposure, at that time seemed rather irregular and not seriously exceeding the limits of experimental error. But after a more detailed scrutiny the deviations of the theory from the experiment turned out to be distinctly systematic, and F. C. Toy's criticism⁽¹⁶⁾ was found to be materially correct by S. E. Sheppard, A. P. H. Trivelli, and R. P. Loveland⁽¹⁷⁾. Finally, L. Silberstein⁽¹⁸⁾ showed mathematically that there is no possible form of the distribution function $f(\epsilon)$ which would give a faithful representation of the experimental findings obtained, with precision, in these laboratories with the grains of a slow process emulsion.

Evidence for a Quantum Theory of X-Ray Exposures.

Th. Svedberg, O. H. Schunk, and H. Anderson⁽¹⁹⁾ had suggested that developable nuclei were formed only when light quanta of sufficient energy struck the grain and were

absorbed within a certain minimum area. On the basis of Zsigmondy's⁽²⁰⁾ investigations about the deposition of gold on colloidal gold particles H. J. Vogler and W. Clark⁽²¹⁾ estimated that about 300 silver atoms are necessary to form a developable centre.

W. Nernst and W. Noddack⁽²²⁾ have given evidence that the impact of one α -particle in a grain produces about 50,000 free silver atoms; while for one quantum of blue-violet light (436–365 $m\mu$ wave-length) not more than one atom of silver is set free. W. Meidinger⁽²³⁾ found that among certain emulsions the great differences in photographic sensitivity for white light were much less for α -particles. He also showed that the sensitizing and desensitizing for light by alkali and acid treatment respectively, which he obtained on certain emulsions, were absent on exposures to α -particles. He suggested, further, that similar relations might be obtained for X-rays as being intermediate in energy concentration between light and α -particles.

That the X-ray latent image is quite different from the latent image produced by visible radiation was mentioned in 1908 by Lüppo-Cramer⁽²⁴⁾. In their studies on sensitivity S. E. Sheppard and A. P. H. Trivelli⁽²⁵⁾ have tested in two ways the ratio of quantum energy to sensitivity. First, a photographic emulsion was prepared with a relatively inert gelatin and also with gelatin sensitized with allyl thio-urea, the grain size distribution being the same in the two cases. Sensitometric comparisons were made with these two emulsions both for white light and for X-rays. The speed values for white light were, respectively, 30 H. and D. and 470 H. and D. There was little difference in the relative speeds (computed similarly from the inertias) of the emulsions when exposed to X-rays. The experiment indicates that no such sensitizing for X-rays is obtained by formation of nuclei containing silver sulphide as is obtainable for white light. Secondly, the same effect was found with the chromic acid treatment. There was a pronounced desensitizing effect for blue light, and this was practically negligible for X-rays. The quantum energies applied at a selected mean wave-length were:

Blue light at about 4000 Å.U. : $h\nu = 4.92 \times 10^{-12}$,

X-rays at 0.275 Å.U. : $h\nu = 7.16 \times 10^{-8}$.

W. Nernst and W. Noddack⁽²⁶⁾ computed that an X-ray quantum of about 0.5 \AA.U. liberates about 1000 silver atoms in a silver halide grain. This is much more than is necessary to produce developability. The Compton effect is regarded as strong evidence for the discrete structure of X-ray radiation. If, therefore, every absorbed X-ray quantum produces a centre of developability independent of the sensitivity specks for the blue-violet exposure, the original simple form of Silberstein's quantum theory of exposure should hold for X-rays. The experimental investigation of this conclusion was supported by two other considerations.

In 1915 Lüppo-Cramer⁽²⁷⁾ discovered evidence of an intensification of the latent image by hydrogen peroxide. It was found by E. P. Wightman, A. P. H. Trivelli, and S. E. Sheppard⁽²⁸⁾, in the course of a study of the action of hydrogen peroxide on photographic plates on which the silver halide grains were spread in a single layer, that the number of developed grains in unit-area affected by light followed by hydrogen peroxide treatment was greater than the sum of those developed in unit area which were acted on separately by light and hydrogen peroxide.

This work was followed by an extensive investigation of the phenomenon by E. P. Wightman and R. F. Quirk⁽²⁹⁾, and W. C. Bray and R. S. Livingston⁽³⁰⁾ showed that hydrogen peroxide reacts with bromide and hydrogen ions to give bromine and water; the bromine can react with more peroxide to give again bromide and hydrogen ions and oxygen. Lüppo-Cramer⁽³¹⁾ had discovered that dilute bromine solution causes latent fog on a photographic plate. E. P. Wightman⁽³²⁾ found that three minutes' treatment with bromine water, 1 : 200,000, caused not only slight latent fog but also a fair intensification of the latent image.

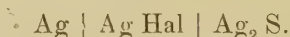
All photographic emulsions contain more or less free potassium bromide which gives bromine with hydrogen peroxide. K. C. D. Hickman⁽³³⁾ obtained evidence that while in bulk bromine reacts with the silver sulphide of the sensitizing speck to give silver bromide, sulphuric acid, and hydrobromic acid; on the other hand, when formed in limited quantity by the photochemical decomposition of silver bromide grains, as in a photographic exposure, it may react with silver sulphide in such a way as to give rise to metallic silver instead of silver bromide, and, possibly

in greater proportion than one silver atom for each silver halide pair decomposed. Silver is presumed to be more effective than its equivalent of silver sulphide in producing developability. It was shown by R. H. Lambert and E. P. Wightman⁽³⁴⁾ that Hickman's hypothesis was thermodynamically plausible.

It is obvious that if the X-ray latent image is a pure silver speck of about 1000 to 2000 silver atoms, there is no possibility of an intensification of the X-ray latent image by hydrogen peroxide, provided the given reaction holds. E. P. Wightman and R. F. Quirk⁽³⁵⁾ were able to show experimentally with an Eastman speedway and with an Eastman process-plate that this prediction was correct.

The other consideration was a plausible explanation of the Luther-USchkoff phenomenon. In 1903 R. Luther and W. A. Uschkoff⁽³⁶⁾ discovered that the latent image of X-rays on photographic plates can be made visible by exposing the plate to daylight if the previous X-ray exposure is sufficient, but still kept below the limits of directly detectable visibility. This phenomenon is explicable by the combination of the concentration speck theory and the quantum theory of X-ray exposure.

The concentration speck theory, as modified by Trivelli⁽³⁷⁾, regards the sensitivity speck on the silver halide grains as an amicroscopical Becquerel cell of the structure



B. H. Carroll and D. Hubbard⁽³⁸⁾ have shown that, in addition to silver sulphide in colloidal state, colloidal silver may act as a sensitivity speck. It is well known that silver against silver in an electrolyte may show a potential difference if the constitution of both silver electrodes is different. For instance, two pieces from the same silver wire show a potential difference if one of these pieces is bent and the other left straight. The strain in one of the silver electrodes is sufficient to produce a potential difference. It is, therefore, quite possible that colloidal silver particles introduced on the surface of the silver halide grain with the photochemical liberated silver form Becquerel cells of the structure



Instead of colloidal silver it may also be a silver speck

formed by an absorbed X-ray quantum, which, after a short induction period, may form a Becquerel cell of the structure



It cannot be expected that these cells will produce the same powerful concentration action as a silver sulphide electrode will, because the potential difference between the electrodes will be much smaller. After the exhaustion of the concentration action of these specks they act as weak spots in the crystal lattice of the silver halide, and continue to grow slowly by prolonged daylight exposure.

We may, therefore, in all probability regard the Luther-Uschko effect as the result of an introduction of new sensitivity centres for daylight exposure on the silver halide crystals of a photographic emulsion by the absorbed X-ray quanta.

All these considerations together led to a renewed investigation of the quantum theory of X-ray exposure on photographic emulsions.

Experimental Details.

The experimental test of the quantum-theory formula requires an investigation of both factors (n and a) of the exponent. For the choice of a suitable photographic emulsion it must be determined which factor is more important—the exposure or the size of the projective area of the grain. For one-grain-layer plates the range of available exposures is very small for X-rays. With fully developed grains X-ray exposures very soon reach high contrast values. We used a pure silver bromide emulsion, for reasons to be discussed later, with a wide range of different grain sizes. The size-frequency curve of this emulsion is given in Pl. X. fig. 1. The classification of the larger grains becomes less reliable with the applied rule method⁽³⁹⁾. The largest grains beyond class 20, therefore, were omitted from the investigation. The classes were

Class	1	=	0.1–0.3	μ^2 ,
„	2	=	0.3–0.6	μ^2 ,
„	3	=	0.6–0.9	μ^2 ,

Class	20	=	5.8–6.0	μ^2 ,

giving a sufficient range for testing.

From this emulsion one-grain-layer plates were made and exposed to X-rays from a water-cooled Coolidge tube running at 85,000 volts, at a distance of 80 cm. between the target of the tube and the photographic plate. The exposures were made in strips on the plate in powers of 2 ratio and the time of every exposure regulated by hand, which makes n less reliable. After exposure the plates were developed for seven minutes in the following developer (4 times diluted) :

Hydroquinone	5.5 grams.
Sodium sulphite (anhydr.)	50.0 „
Sodium carbonate	50.0 „
Potassium bromide	0.02 „
Water	to 1 litre.

As shown in Pl. X. fig. 2, where a photomicrograph of one of the exposures at a magnification of $2500\times$ is reproduced, this developer develops pure silver bromide grains of the same shape and size as the original grain. This simplified the method of investigation considerably. In previous investigations we had used a method first applied by Th. Svedberg ⁽⁴⁰⁾, in which the original grains on a one-grain-layer plate were first counted and classified. Then a plate coated similarly was used for exposure and development; the developed grains were removed by chromic acid and sulphuric acid, and the remaining grains were counted and classified. If narrow classes of grains were required this procedure had to be repeated several times and the results averaged.

The development of pure silver bromide emulsions with a hydroquinone developer greatly simplifies this method. We are able to determine immediately, on one spot, which grains were affected and which remained intact. One plate is insufficient, and this eliminates development deviations and differences in the distribution of grains on the different plates.

In the photomicrograph Pl. X. fig. 1, which shows only undeveloped grains, there are a few black grains among the undeveloped grains. This is due to their thickness, and a distinction between these grains and the developed grains can be detected very easily on the negatives. They show an internal structure and are not entirely black.

Three different exposures were investigated. The second exposure was twice as great as the first, and the third was twice as great as the second. For every exposure 300 fields at a magnification of $10,000\times$ were used. From a series of ten different exposures these three were microscopically the only useful fields. One of these fields was omitted because of the erratic results, which we believe to be caused by the influence of some contamination (occurring during the setting) of the gelatin of the one-grain-layer plate on a spot of that exposure region.

Treatment of Data.

If the probability p of a grain of size a being affected by the exposure n is

$$p = 1 - e^{-na},$$

then the number k of grains actually affected out of a total of N grains, all of size a , is

$$k = Np \pm N \text{ (P.D.)},$$

where (P.D.), the probable deviation, is given by

$$\text{(P.D.)} = 0.477 \sqrt{\frac{2p(1-p)}{N}}.$$

Unless the deviation from the calculated data is more than 2.5 or 3 times greater than (P.D.) the agreement can be considered fairly satisfactory. All observed data falling within the limits of the probable deviation can be regarded as being in perfect agreement with the theoretical values.

For the determination of the calculated data we use, instead of the size a of the grain, the average size \bar{a} of the class of grains—that is to say, neglecting the small correction for the finite width of the classes *, we put

$$p = 1 - e^{-n\bar{a}}.$$

This gives

$$\log(1-p) = -n\bar{a},$$

$$\log(1-p) = -Mn\bar{a},$$

$$\frac{-\log(1-p)}{\bar{a}} = Mn = \text{constant} = C$$

(i. e., constant within an exposure step), where $M = 0.4343$.

* Formulated in a previous paper.

Discussion of Data.

It was found as an average for

$$\text{Step 4: } C_4 = 0.0427,$$

$$,, \quad 3 : C_3 = 0.0832.$$

TABLE I.

Step 4.

$$C_4 = 0.0422.$$

Class.	\bar{a} .	N.	$100 \frac{k}{N}$ obs.	$100 \frac{k}{N}$ calc.	100 (P.D.).	100 Δ .	$\frac{\Delta}{(P.D.)}$.	C.
1	0.23	4182	0.7	2.2	0.6	1.5	2.5	0.014
2	0.45	3295	3.3	4.3	1.3	1.0	0.8	.032
3	0.75	1821	5.0	7.0	1.8	2.0	1.1	.030
4	1.05	1014	11.2	9.7	1.9	-1.5	0.8	.049
5	1.35	688	17.3	12.3	2.0	-5.0	2.5	.061
6	1.65	532	15.7	14.7	2.6	-0.4	0.3	—
7	1.95	482	19.5	17.3	2.6	-2.2	0.8	.048
8	2.25	408	16.7	19.7	3.2	2.9	0.9	—
9	2.55	350	22.0	21.9	3.2	-0.1	0.03	.042
10	2.85	292	23.1	24.2	3.5	1.1	0.3	.040
11	3.15	252	18.9	26.4	4.2	7.5	1.8	—
12	3.45	229	22.3	28.5	4.3	6.2	1.4	.032
13	3.75	185	23.2	30.5	4.7	7.3	1.6	.031
14	4.05	180	20.0	32.5	5.2	3.3	2.4	—
15	4.35	166	30.8	34.5	4.5	6.3	1.4	.037
16	4.65	159	30.8	36.4	4.6	5.5	1.2	.034
17	4.95	123	41.3	38.2	4.6	-3.1	0.7	.047
18	5.25	128	44.7	39.9	4.4	-4.8	1.1	.049
19	5.55	107	45.8	41.7	4.7	-4.1	0.9	.048
20	5.85	81	55.6	43.4	5.0	-12.2	2.4	.060

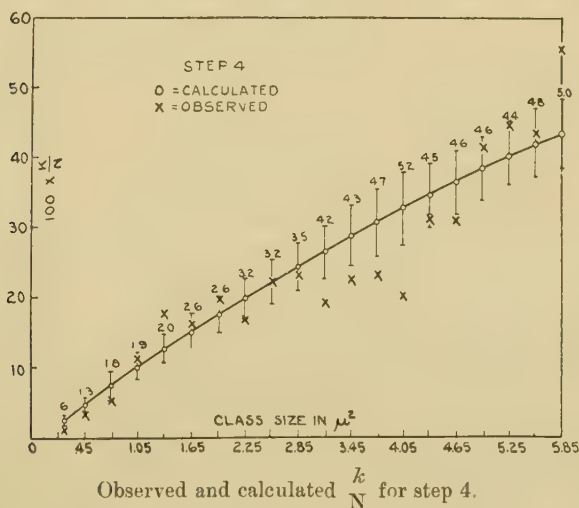
This ratio of C_4 to C_3 represents fairly well the ratio 1 : 2 as it should be according to the given exposure times. We choose for the calculation of the p -values the average of C_4 and $\frac{1}{2}C_3$. Thus we take $C_4 = 0.0422$ and $C_3 = 0.0844$.

In Table I. are given the observed and the calculated values for step 4. Delta represents the difference between these values, and $\frac{\Delta}{(P.D.)}$ expresses how far we may rely on

the results of the comparison as a support of the theoretical considerations.

In fig. 1 are plotted the observed and calculated $\frac{k}{N}$ data for step 4, with the calculated probable deviations represented by vertical strokes. We see that from the twenty data fourteen observations are in perfect agreement with the theoretical requirements; two observations are fairly well represented, and four observations show deviations 2.4-2.5 times greater than the probable deviations, and are thus still fairly satisfactory.

Fig. 1.



In Table II. are given the observed and the calculated $\frac{k}{N}$ data of step 3. In fig. 2 are plotted these data, with the probable deviations. We see that from the twenty observations ten are in perfect agreement with the theoretical requirements, six observations are fairly satisfactory, three observations have deviations which are 2.3, 2.4, and 2.5 times larger than the probable deviation; which means that they are still satisfactory, while only one observation is far off the theoretical value.

This agreement between theory and experiment seems close enough to enable us to assert that the quantum theory of X-ray exposures on photographic plates holds.

The Distribution of the Latent Image.

There are many evidences for the assumption that the latent image produced by visible light on photographic emulsions lies practically on the surface of the silver halide grains⁽⁴¹⁾.

On the other hand, the absorption of X-rays in a silver bromide crystal of a photographic emulsion is negligible.

TABLE II.

Step 3.

 $C_3=0.0844$.

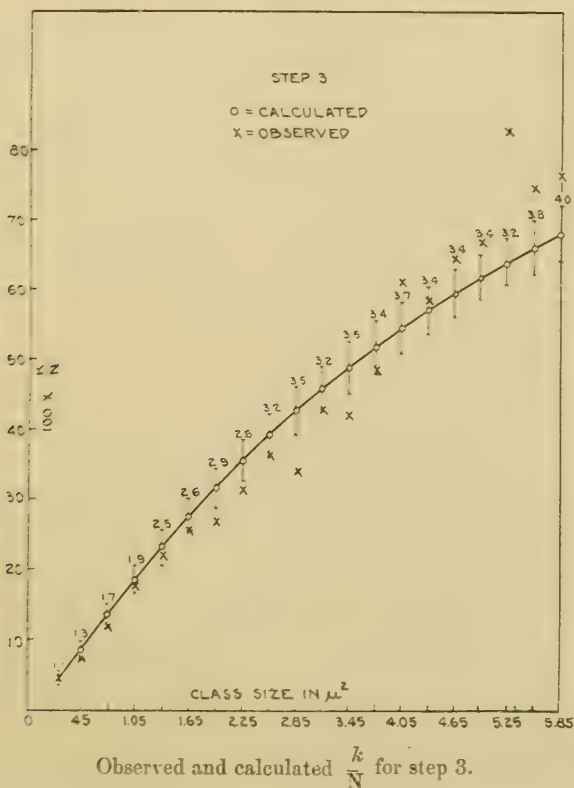
Class.	\bar{a} .	N.	$100 \frac{\bar{x}}{N}$ obs.	$100 \frac{\bar{x}}{N}$ calc.	100 (P.D.).	100 Δ .	Δ (P.D.).	C.
1	0.23	3379	4.4	4.4	1.1	0.0	0.0	0.084
2	0.45	2621	7.3	8.4	1.3	1.1	0.8	.074
3	0.75	1651	11.8	13.6	1.7	1.8	1.1	.073
4	1.05	1036	17.8	18.4	1.9	0.6	0.3	.081
5	1.35	612	21.9	23.1	2.5	1.2	0.5	.079
6	1.65	512	25.5	27.4	2.6	1.9	0.7	.077
7	1.95	428	26.7	31.5	2.9	4.8	1.7	.069
8	2.25	402	32.3	35.4	2.8	3.1	1.1	.075
9	2.55	291	36.2	39.1	3.2	2.9	0.9	.077
10	2.85	266	33.7	42.5	3.5	8.8	2.5	—
11	3.15	252	42.7	45.8	3.2	3.1	1.0	.077
12	3.45	221	42.0	48.8	3.5	6.8	1.9	.069
13	3.75	201	48.4	51.7	3.4	3.3	1.0	.077
14	4.05	137	61.3	54.5	3.7	6.8	1.8	.102
15	4.35	164	58.4	57.1	3.4	1.3	0.4	.087
16	4.65	143	64.8	59.5	3.4	5.3	1.6	.098
17	4.95	139	66.9	61.8	3.4	5.1	1.5	.097
18	5.25	122	82.8	63.9	3.2	18.9	5.9	—
19	5.55	95	74.7	66.0	3.8	8.7	2.3	.107
20	5.85	81	76.5	67.9	4.0	9.5	2.4	.108

on an ordinary photographic film more than 90 per cent of the incident X-ray energy penetrates the emulsion.

Comparing the development of a one-grain-layer plate of a visible-light exposure with one of an X-ray exposure, we noticed a difference. Within a few minutes all day-light-affected grains are developed, and additional development gives development fog, which increases much more slowly than the number of developed grains. The X-ray

affected grains continue to produce developed grains with increasing time of development in gradually changing rate. This led to the conclusion that we have to regard the X-ray latent image as being distributed haphazardly through the entire silver halide grain. This explains the differences R. Wilsey⁴² found in the values of the development factor k for daylight and for X-ray exposures.

Fig. 2.



Summary.

1. Evidence is given for the validity of the quantum theory of X-ray exposure on photographic emulsions.

2. An experimental investigation was made, the observed data were compared with the calculated values, and the principle of the theoretical probable deviation was applied.

3. It was found that there is a close agreement between theory and experiment.

4. The distribution of the X-ray latent image was discussed.

Our thanks are due to Mr. E. C. Jensen for assisting us in the various calculations.

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Rochester, N.Y.

October 7th, 1929.

LXXIII. *Forced Vibrations with combined Viscous and Coulomb Damping.* By J. P. DEN HARTOG *.

I. *Introduction.*

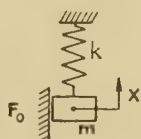
THE free vibrations of a single degree of freedom system affected by a constant friction force are determined by the pair of equations :

$$m\ddot{x} + kx \pm F_0 = 0,$$

of which the solution for any initial condition is well known. When, moreover, a sinusoidal disturbing force is acting on the mass, a steady periodic non-harmonic motion will be set up after a sufficient length of time.

It is evident that in case the friction force is small with respect to the disturbing force amplitude, the ensuing motion will be continuous, while for large values of the friction force a single cycle of the motion may consist of regions of motion

Fig. 1.



and regions of standstill. In this paper an analytical solution has been obtained for motions without standstill, *i. e.* for sufficiently small damping †. It is found that this solution is valid for such values of the friction and the frequency as are ordinarily met in engineering applications.

II. *Only Coulomb Damping.*

The differential equation (of fig. 1) is

$$m\ddot{x} + kx \pm F_0 = P_0 \cos(\omega t + \phi), \quad . \quad . \quad . \quad (1)$$

where the upper (+) sign holds for upward motions ($\dot{x} > 0$) and the lower (−) sign for $\dot{x} < 0$. The quantity ϕ is a parameter as yet devoid of meaning. Introducing the notations :

$$F_0/k = af, \quad P_0/k = a, \quad k/m = \omega_n^2,$$

* Communicated by R. V. Southwell, F.R.S.

† An approximate solution, based on a graphical method for values $\omega/\omega_n < 1.1$, including both motions with and without stops, is described by W. Eckolt, *Zt. f. techn. Physik*, vii. p. 226 (1926).

the equation for $\dot{x} < 0$ can be written as

$$\ddot{x} + \omega_n^2(x - x_f) = a\omega_n^2 \cos(\omega t + \phi). \quad (2)$$

In order to obtain a periodic solution for the motion, the following boundary conditions are imposed:—

$$\left. \begin{aligned} t = 0, \quad x = x_0, \quad \dot{x} = 0, \\ t = \pi/\omega, \quad x = -x_0, \quad \dot{x} = 0. \end{aligned} \right\} \quad (3)$$

The motion thus defined for the downward half cycle between the maxima $+x_0$ and $-x_0$ has to be completed by an upward motion which is identical with the previous half except for a negative sign. This describes a motion which has the same period as the impressed force and therefore can be called a forced vibration. It is seen from (2) and (3) that ϕ represents the “phase-angle” by which the force leads the motion. Since the motion is non-harmonic, it is clear that this “phase-angle” applies only to the *maxima* of force and motion, and that in general the phase between the zeros of force and motion will be different from ϕ .

The general solution of (2) is

$$x = C_1 \sin \omega_n t + C_2 \cos \omega_n t + \frac{\omega_n^2}{\omega_n^2 - \omega^2} a \cos(\omega t + \phi) + x_f. \quad (4)$$

The four conditions (3) can be satisfied by assigning certain values to C_1 , C_2 , x_0 , and ϕ . Eliminating C_1 and C_2 from (4) by means of the two first conditions (3), leads to

$$\begin{aligned} x = x_0 \cos \omega_n t + x_f(1 - \cos \omega_n t) \\ + \frac{a\beta^2}{\beta^2 - 1} \left[\cos \phi \{ \cos \omega t - \cos \omega_n t \} \right. \\ \left. + \sin \phi \left\{ \frac{\sin \omega_n t}{\beta} - \sin \omega t \right\} \right], \quad (4a) \end{aligned}$$

where

$$\beta = \omega_n/\omega.$$

Substitution of the last two conditions in this gives two equations:

$$\left. \begin{aligned} A \cos \phi + B \sin \phi + C = 0, \\ P \cos \phi + Q \sin \phi + R = 0, \end{aligned} \right\} \quad (5)$$

where

$$A = -a \cdot \frac{\beta^2}{\beta^2 - 1} (1 + \cos \beta\pi).$$

$$B = +a \frac{\beta}{\beta^2 - 1} \sin \beta\pi,$$

$$P = +a\omega_n \frac{\beta^2}{\beta^2-1} \cdot \sin \beta\pi,$$

$$Q = +a\omega_n \frac{\beta}{\beta^2-1} (1 + \cos \beta\pi),$$

$$C = +x_0(1 + \cos \beta\pi) + x_f(1 - \cos \beta\pi),$$

$$R = (x - x_0)\omega_n \sin \beta\pi.$$

From (5) we get

$$\cos \phi = \frac{BR - CQ}{AQ - PB}; \quad \sin \phi = \frac{CP - AR}{AQ - PB},$$

or, after substitution of the values for A etc.,

$$\left. \begin{aligned} \cos \phi &= \frac{x_0}{a} \cdot \frac{\beta^2 - 1}{\beta^2}, \\ \sin \phi &= -\frac{x_f}{a} \cdot \frac{\beta^2 - 1}{\beta^2} \cdot \frac{\beta \sin \beta\pi}{1 + \cos \beta\pi}. \end{aligned} \right\} \quad \cdot \quad \cdot \quad (6)$$

Eliminating ϕ and solving for the amplitude x_0 , we have

$$x_0 = a \sqrt{\left(\frac{\beta^2}{\beta^2-1}\right)^2 - \left(\frac{x_f}{a}\right)^2 \cdot \left(\frac{\beta \sin \beta\pi}{1 + \cos \beta\pi}\right)^2} \quad \cdot \quad \cdot \quad (7)$$

Introducing the notations :

$$V = \frac{\beta^2}{\beta^2-1} = \frac{\omega_n^2}{\omega_n^2 - \omega^2} = \text{"response function,"}$$

$$U = \frac{\beta \sin \beta\pi}{1 + \cos \beta\pi} = \text{"damping function,"}$$

the results (6) and (7) can be written as

$$\sin \phi = -\frac{x_f}{a} \cdot \frac{U}{V}; \quad \cos \phi = +\frac{x_0}{a} \cdot \frac{1}{V}, \quad \cdot \quad \cdot \quad (6a)$$

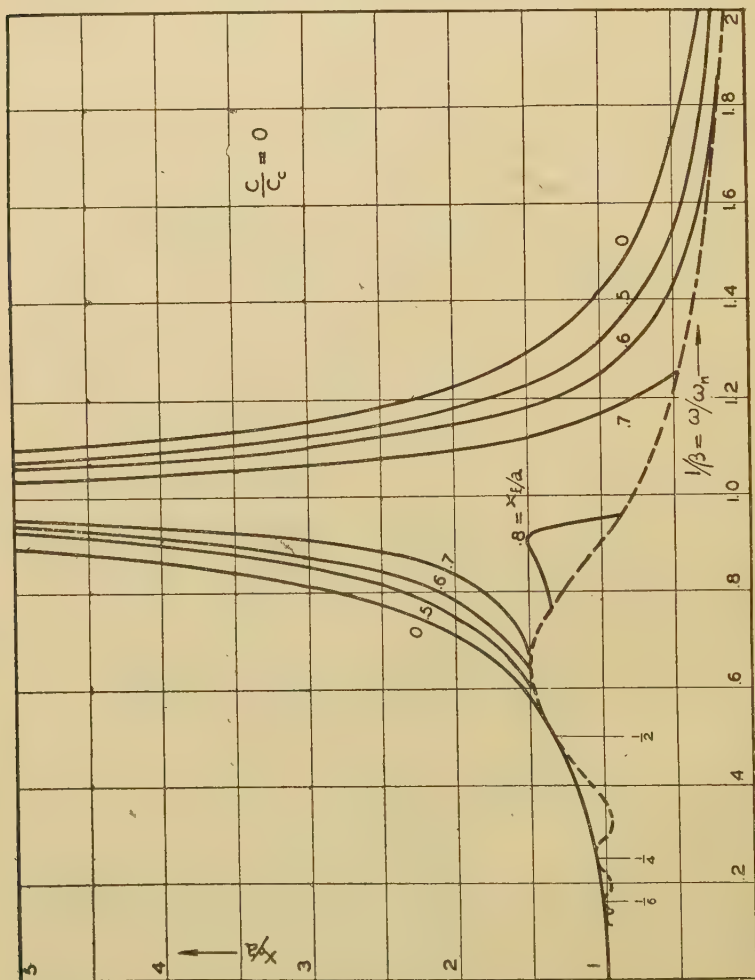
$$x_0 = a \sqrt{V^2 - \left(\frac{x_f}{a}\right)^2 U^2} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7a)$$

It is seen that the amplitude x_0 is not proportional to the impressed force $P_0 (=ak)$. The influence of the damping appears in the formula as the ratio of the friction force to the impressed force : $x_f/a = F_0/P_0$.

III. *Validity of Solution.*

This solution is valid only when $\dot{x} \leq 0$ during the interval $0 \leq t \leq \pi/\omega$. Substituting (6a) and (7a) into (4a), and differentiating, the condition can be transformed to

Fig. 2.



Amplitudes of vibration with Coulomb damping.

$$\frac{x_0}{x_f} > \beta^2 \left[\frac{\beta \sin \beta \omega t + U (\cos \omega t - \cos \beta \omega t)}{\beta^2 \sin \omega t} \right] \quad (8)$$

for $0 \leq t \leq \pi/\omega$

or $\frac{x_0}{x_f} > \beta^2 \cdot S,$

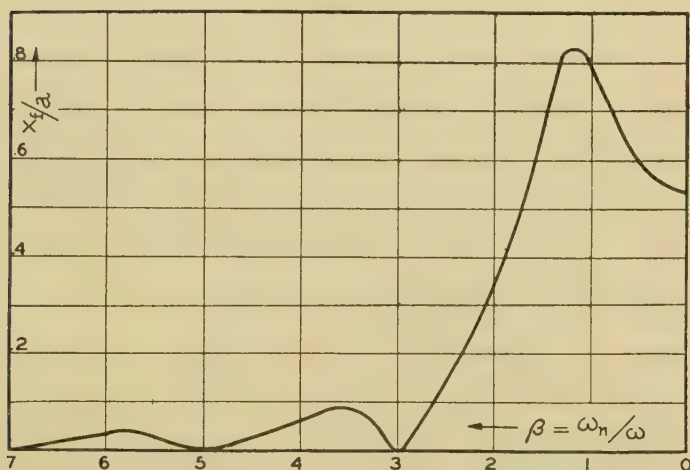
where S denotes the maximum value of the bracket during that time-interval. For $t=0$ the bracket is equal to unity, and numerical calculations have shown that in quite many cases this is also the maximum value. From (7) and (8) we deduce

$$\frac{x_0}{a} \geq \sqrt{\frac{V^2}{1 + (U/S\beta^2)^2}} \cdot \cdot \cdot \cdot (9)$$

and

$$\frac{x_f}{a} \leq \sqrt{\frac{V^2}{(S\beta^2)^2 + U^2}} \cdot \cdot \cdot \cdot (10)$$

Fig. 3.



Damping determining boundary of non-stop motion.

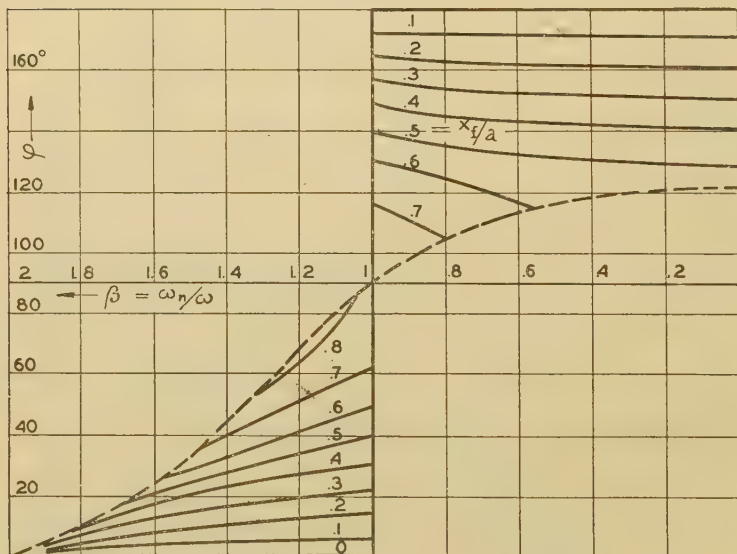
Fig. 2 shows a graphical representation of these results. The dotted line is the boundary (equation (9)), below which only motions with stops occur. It is seen that for frictions $x_f/a < \pi/4$ the amplitude at resonance becomes infinitely large.

The relation (10) is represented by fig. 3, so that for frictions below this line the solutions (6) and (7) are valid and motions without stops can exist, while for higher frictions this is not the case. Comparing fig. 3 with the dotted boundary of fig. 2, it is seen that for even integer values of $\beta (= \omega_n/\omega)$ the amplitude of the motion (and the phase-angle) are independent of the amount of friction up to the limit set by fig. 3. For odd integer values of β the

smallest friction will cause stops in the motion and a considerable decrease in the amplitude. It might be said that for odd β the friction is "infinitely efficient" in reducing the amplitude, while for even β it is "infinitely inefficient."

Fig. 4 gives the results (6a) for the phase-angle, showing the peculiarity of jumps in the angle at resonance for any friction up to $x_f/a = \pi/4$.

Fig. 4.



Phase-angle diagram with pure Coulomb damping.

IV. Combined Viscous and Coulomb Damping.

The analysis for this case is quite analogous to the previous one. The differential equations are

$$m\ddot{x} + kx + c\dot{x} \pm F_0 = P_0 \cos(\omega t + \phi), \quad (11)$$

or for the downward stroke only,

$$\ddot{x} + \omega_n^2(x - x_f) + \frac{c}{m} \dot{x} = a\omega_n^2 \cos(\omega t + \phi), \quad (11a)$$

with the boundary conditions (3).

Using the abbreviations :

$$p = \sqrt{\omega_n^2 - \frac{c^2}{4m^2}} = \omega_n \sqrt{1 - \left(\frac{c}{c_c}\right)^2},$$

$$q = \sqrt{\left(\frac{1}{V}\right)^2 + \left(\frac{2}{\beta} \cdot \frac{c}{c_c}\right)^2},$$

where

$$c_c = \text{critical damping} = 2m\omega_n,$$

the general solution of (11a) can be written

$$x = e^{-\frac{ct}{2m}} [C_1 \cos pt + C_2 \sin pt] + \frac{a}{q} \sin(\omega t + \epsilon) + x_f, \quad (12)$$

with

$$\tan(\phi - \epsilon) = \frac{c\omega}{k - m\omega^2} = \frac{2V}{\beta} \cdot \frac{c}{c_c}. \quad (12a)$$

Now C_1 , C_2 , x_0 , and ϕ are determined so as to satisfy the four conditions (3) in exactly the same manner as before, though the calculation becomes rather involved.

The result can be conveniently presented in the following form :—

$$\frac{x_0}{a} = -G\left(\frac{x_f}{a}\right) + \sqrt{\frac{1}{q^2} - H^2\left(\frac{x_f}{a}\right)^2}, \quad (13)$$

$$\sin \epsilon = -qH \frac{x_f}{a}; \quad \cos \epsilon = q \left[\frac{x_0}{a} + G \cdot \frac{x_f}{a} \right], \quad (14)$$

the first of which gives the amplitude directly, while the second, in conjunction with (12a), allows of an easy numerical calculation of the phase-angle ϕ .

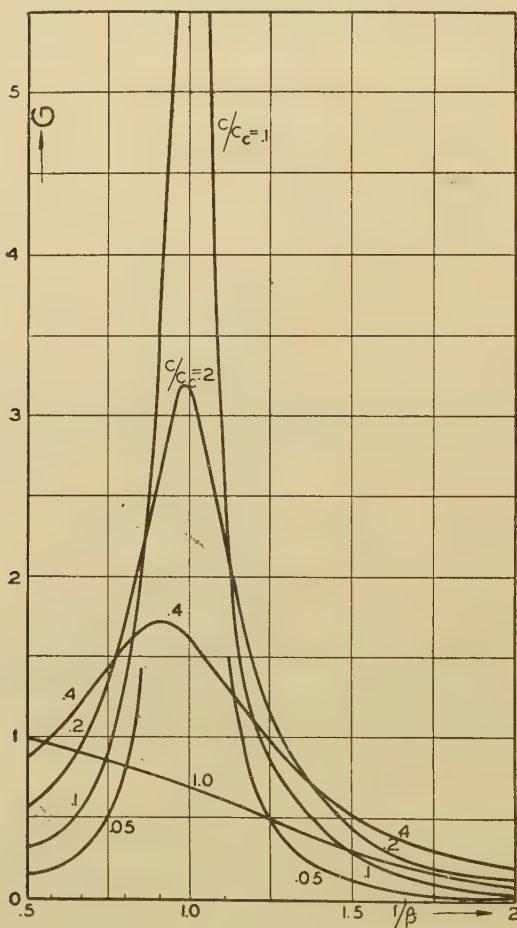
In these expressions G and H are functions of the viscous damping c/c_c and of the frequency β :

$$\left. \begin{aligned} G &= \frac{\sinh(\beta\pi c/c_c) - \frac{c/c_c}{\sqrt{1 - (c/c_c)^2}} \cdot \sin \beta\pi \sqrt{1 - (c/c_c)^2}}{\cosh(\beta\pi c/c_c) + \cos \beta\pi \sqrt{1 - (c/c_c)^2}}, \\ H &= \frac{\beta}{\sqrt{1 - (c/c_c)^2}} \cdot \frac{\sin \beta\pi \sqrt{1 - (c/c_c)^2}}{\cosh(\beta\pi c/c_c) + \cos \beta\pi \sqrt{1 - (c/c_c)^2}}. \end{aligned} \right\} \quad (15)$$

It is seen that in the absence of Coulomb damping, (13) reduces to $x_0/a = 1/q$, which is the well-known result for viscous damping only. Likewise in this case the auxiliary

angle ϵ becomes zero, so that the phase (12a) coincides with the well-established theory.

Fig. 5.

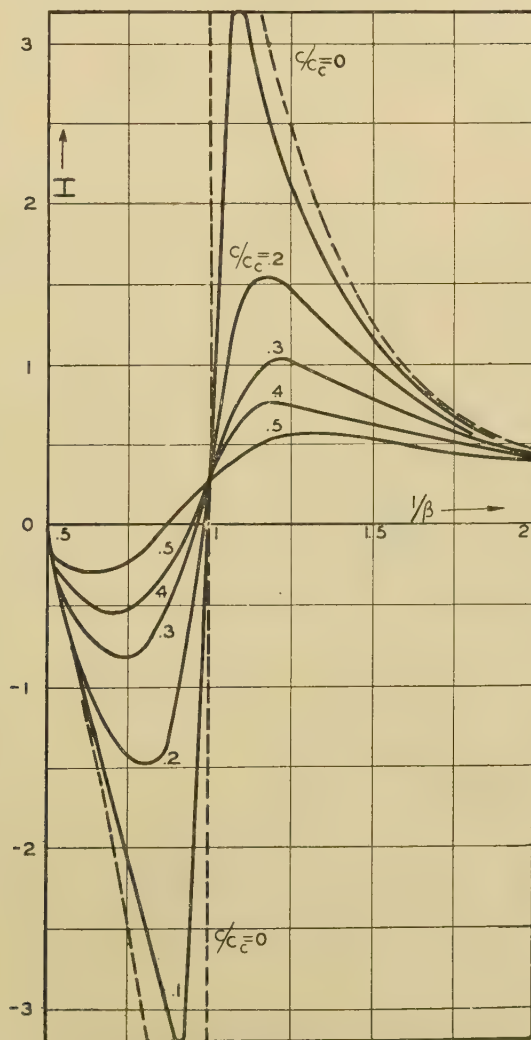


Graph of the G function.

It is of interest to note that for $c/c_c = 0$ the G function is zero for all values of β , except $\beta = 1$, where G tends to infinity. The H function reduces to V for $c/c_c = 0$. Since these two functions play an important role in the numerical

calculations, they are shown in figs. 5 and 6 for various values of c/c_c .

Fig. 6.



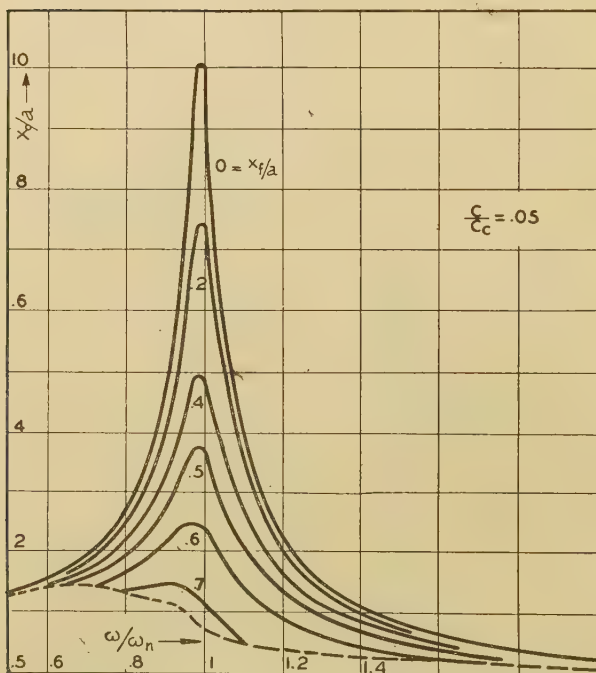
Graph of the H function.

The numerical results of the amplitudes of vibration for six values of c/c_c are represented in figs. 7 to 12. The condition of validity of the solution, $\dot{x} \leq 0$, becomes

$$\frac{x_0}{x_f} \geq \frac{e^{-\frac{ct}{2m}}}{\sin \omega t} \cdot \left\{ \left(\frac{p}{\omega} + \frac{c^2}{4m^2 p \omega} \right) (1+G) \sin pt \right. \\ \left. + H \left(\frac{c}{2pm} \sin pt - \cos pt \right) \right\} + H \cotg \omega t - G$$

for $0 \leq t \leq \pi/\omega. \quad . \quad . \quad . \quad . \quad . \quad (16)$

Fig. 7.



Amplitudes with mixed damping.

For $t=0$ this expression reduces to

$$\frac{x_0}{x_f} \geq -G + 2H\beta c/c_c + \beta^2(1+G), \quad . \quad . \quad (17)$$

which quite often is also the maximum value of (16). In fact, for any $\beta < 2$ this is the case. Let S_1 denote the ratio

Fig. 8.

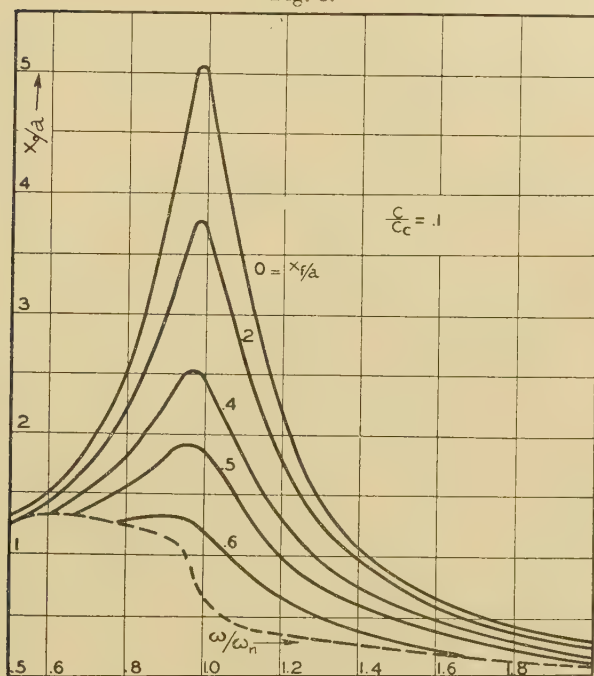


Fig. 9.

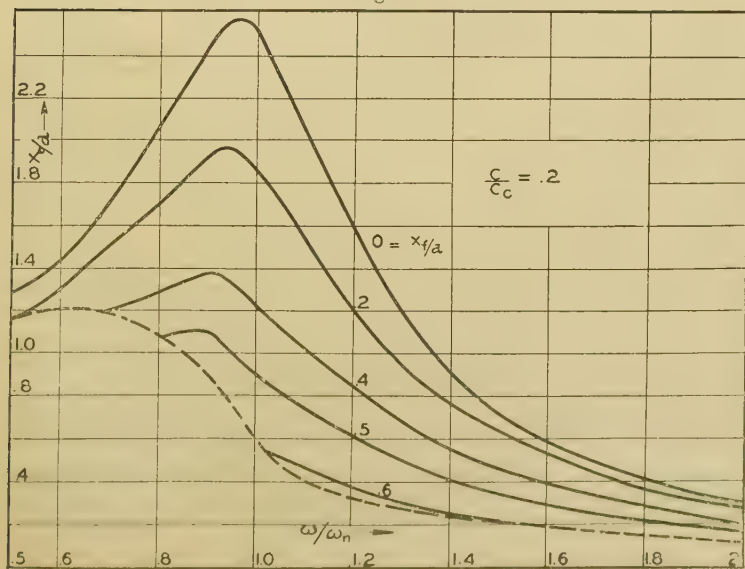


Fig. 10.

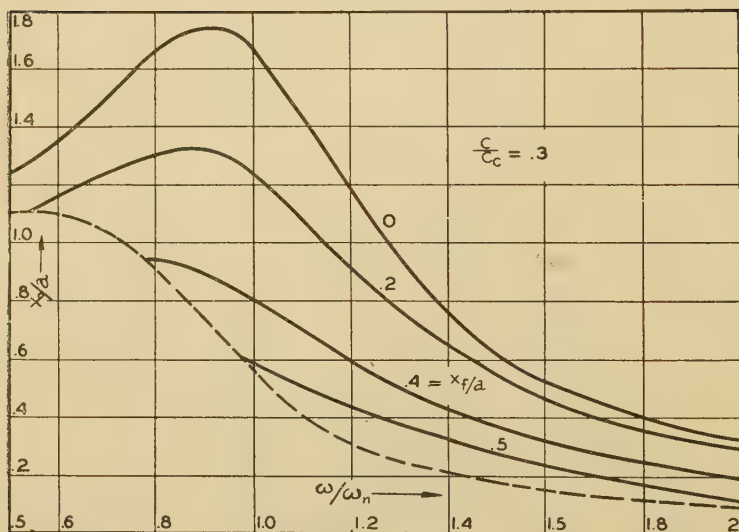
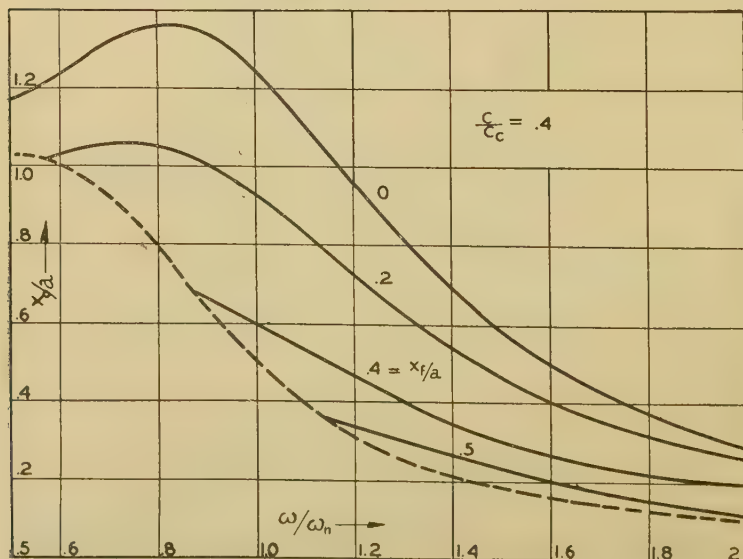


Fig. 11.

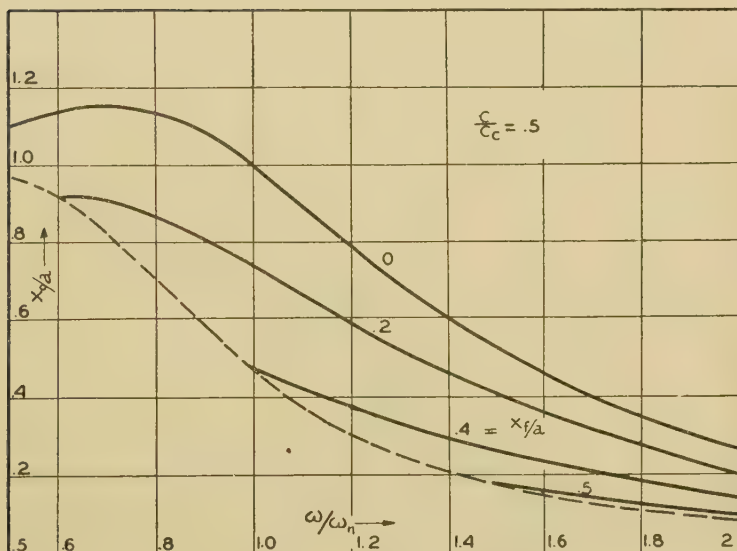


of the maximum of (16) and (17), which is equal to unity for $\beta < 2$. Then we have

$$\frac{x_0}{a} \geq \frac{S_1(I-G)}{q \sqrt{H^2 + \{S_1 I + (1-S_1)G\}^2}},$$

$$\frac{x_f}{a} \leq \frac{1}{q \sqrt{H^2 + \{S_1 I + (1-S_1)G\}^2}},$$

Fig. 12.



where

$$I = 2H\beta c/c_c + \beta^2(1+G).$$

With these formulæ the dotted lines in figs. 7-12 have been calculated.

The phase-angle diagram for $c/c_c = .1$ is given in fig. 13. Since the amplitudes at resonance are finite, no discontinuity in the angle occurs. It is noted that the angle at resonance is quite near to 90° , while for other frequencies the phase-angle differs considerably from that of a motion with viscous damping only. The greatest difference occurs at $\beta = 0$ or $\omega_n = 0$, which is of importance for engineering applications (Lanchester torsional vibration damper).

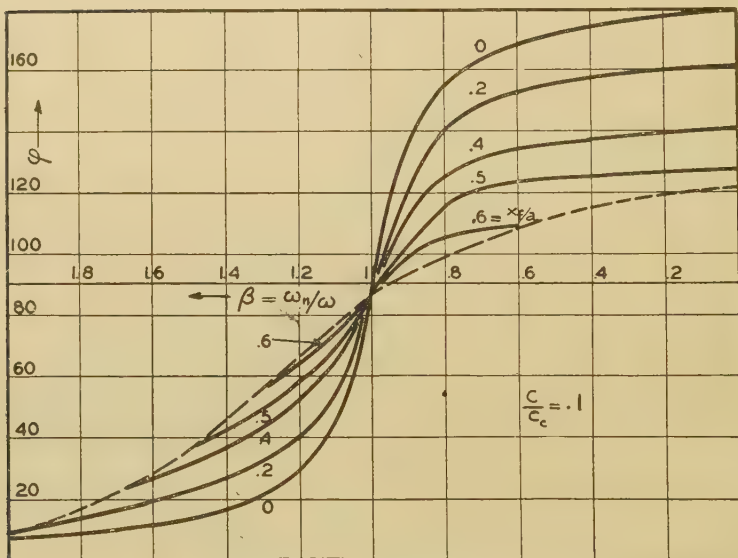
Due to the fact that $\phi \approx 90^\circ$ at resonance, the amplitude at that point for combined damping can be calculated with a fair approximation from an energy consideration. Assuming the motion sinusoidal, the work input per cycle by the force $P_0 \sin \omega t$ is

$$\pi P_0 x_0.$$

The friction force is $F_0 + cx_0\omega \sin \omega$ and its work absorption per cycle is

$$\int_0^T (F_0 + cx_0\omega \sin \omega t) \cdot v dt = 4F_0x_0 + c\omega x_0^2\pi.$$

Fig. 13.



Phase-angles with mixed damping.

Equating the two, we get

$$x_0 = \frac{P_0}{c\omega} \left[1 - \frac{4}{\pi} \frac{F_0}{P_0} \right]. \quad . \quad . \quad . \quad (17)$$

The difference of this expression with the exact solution naturally increases with the amount of damping of either kind: for $c/c_c = .5$ and $x_f/a = .4$ it is only 3 per cent. The degree of approximation can be visualized from the fact that for $\beta = 1$, G is large and H small, so that (13) reduces to

$\frac{1}{q} - G\left(\frac{x_f}{a}\right)$. Moreover, at resonance both $1/q$ and G are nearly proportional to c/c_c .

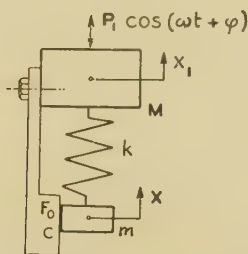
At frequencies other than resonance no simple rule for the amplitude can be given; then recourse has to be taken to figs. 7 to 12.

V. Other Problems to which the Solution applies.

1. If in fig. 1 no external force be acting on the mass, but the upper end of the spring be moved $a_0 \cos(\omega t + \phi)$, it can be verified that the above solution holds for the absolute motion of the mass, when only a be replaced by a_0 .

2. If in fig. 1 the rubbing wall be tied to the upper end of the spring and this end with the wall be subjected to the

Fig. 14.



motion $a_0 \cos(\omega t + \phi)$, the above solution holds for the relative motion between mass and wall, if only a be replaced by a_0/β^2 .

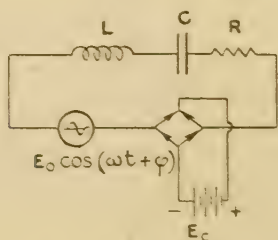
3. Fig. 14 represents a two-mass system with relative damping and a force $P_1 \cos(\omega t + \phi)$ acting on the mass M . It can be shown that all previous results apply to the relative motion $x - x_1 = y$, if only m be replaced by $mM/(m + M)$ and P_0 by $P_1 \cdot m/(M + m)$. The absolute motions of m and M can be found to be

$$\left. \begin{aligned} x &= \frac{M}{M+m} y - \frac{P_1}{\omega^2(M+m)} \cos(\omega t + \phi), \\ x_1 &= -\frac{m}{M+m} y - \frac{P_1}{\omega^2(M+m)} \cos(\omega t + \phi). \end{aligned} \right\} \quad (18)$$

4. It is evident that all the above problems have torsional equivalents when masses are replaced by moments of inertia, displacements by angles, etc.

5. An electrical problem leading to the same differential equation is shown in fig. 15. The four rectifiers keep the constant battery voltage always directed against the current. The previous results hold if the velocity \dot{x} be replaced by the

Fig. 15.

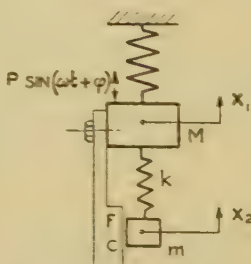


current i , the mass m by the inductance L , the spring constant k by the inverse capacity $1/C$, the viscous friction c by the resistance R , the constant friction F_0 by the battery voltage E_c , and the force amplitude P_0 by the voltage amplitude E_0 .

VI. *Systems with many Degrees of Freedom.*

The method outlined above is not restricted to systems with a single degree of freedom, but can be successfully applied to problems of greater complication. As an example

Fig. 16.



let us consider fig. 16. Two simultaneous differential equations can be written down, conveniently in the variables x_1 and $x_1 - x_2 = x_r$. When only one-half stroke of the motion is considered, there will be no ambiguity in the sign of the Coulomb damping term. As before, a parameter ϕ is written

in the expression for the disturbing force. Since the differential equations are linear and of the second order, their solution can be written down involving four constants. Let the initial conditions be

$$t=0; \quad x_1=x_{10}; \quad \dot{x}_1=\dot{x}_{10}; \quad x_r=x_{\max.}; \quad \dot{x}_r=0.$$

With these conditions the integration constants can be eliminated, and the solution appears as a function of four parameters— x_{10} , \dot{x}_{10} , $x_{\max.}$, and ϕ —which can be determined by four conditions at $t=\pi/\omega$, namely

$$x_1=-x_{10}, \quad \dot{x}_1=-\dot{x}_{10}, \quad x_r=-x_{\max.}, \quad \text{and} \quad \dot{x}_r=0.$$

The solution thus obtained is valid only if

$$x_r \leq 0 \quad \text{for} \quad 0 \leq t \leq \pi/\omega.$$

In a similar manner the steady-state solutions for systems of any number of degrees of freedom involving both viscous and Coulomb damping can be determined.

Acknowledgement.

The author's thanks are due to the University of Pittsburgh for permission to publish this work, which represents an abstract of a doctor's dissertation.

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LXXIV. *The Psychophysical Law.*—I. *The Sense of Vision.*

By P. A. MACDONALD, *M.Sc., Hudson Bay Fellow, and*
JOHN F. ALLEN, *B.A., Research Assistant, Department of*
Physics, University of Manitoba, Winnipeg, Canada *.

IT has long been known that the physical intensity of a sensory stimulus may be increased by an amount so small that the increment does not cause a corresponding increase in the sensation evoked by the stimulus. Denoting the physical intensity of the stimulus by I , and the small increment by δI , experiment has shown that δI may be increased to a critical value such that a just perceptible increase in the sensation results. This value of δI is

* Communicated by Prof. Frank Allen.

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known as the differential threshold, and is usually denoted by ΔI .

The variation of the magnitude of ΔI with reference to different values of I was first seriously investigated by Weber, who concluded that a simple relation existed between these quantities, which is expressed by the equation

$$\frac{\Delta I}{I} = c,$$

where c is a constant.

Extending Weber's work, an attempt to establish a relation between the intensity of a physical stimulus and the corresponding sensation evoked was made by Fechner, who used Weber's relation as the basis of his development of the subject.

"Fechner's Law," following Parsons's treatment*, states that "the sensation varies as the logarithm of the stimulus, *i. e.* the sensation changes in arithmetical proportion as the stimulus increases in geometrical proportion.

"Stated algebraically, if S is the measure of a sensation and δS the just appreciable difference, I the measure of the stimulus and δI a small increment, then

$$\delta S = k \frac{\delta I}{I} \quad (\text{Weber's law}),$$

where k is a constant; therefore, on the questionable assumption that it is permissible to integrate small finite quantities (δs etc.),

$$\begin{aligned} S &= k \int \frac{dI}{I} \\ &= k \log I + k' \quad (\text{Fechner's law}), \end{aligned}$$

where k' is another constant."

Both laws have been subjected to an immense number of experimental investigations in the various senses. It is only in the sense of vision, however, that the researches have reached a high degree of accuracy, the best work, by general consent, having been carried out by König†. As König's ability and prolonged experience in visual measurements preclude the likelihood of errors in his

* Sir J. H. Parsons, 'Colour Vision,' 2nd ed. p. 23

† A. König, *Physiol. Optik*, 1903.

measurements, only his work will be considered in this treatment, and taken as typical of the best experimental work and procedure.

König, keeping his eyes in darkness adaptation, used as a stimulus a patch of light viewed through a suitable ocular. The upper half of the patch being maintained at a definite brightness, I , the intensity of the lower half was varied by nicol prisms until it was just perceptibly brighter than

TABLE I.
König's Data.

$\lambda=6700 \text{ \AA.}$		$\lambda=5050 \text{ \AA.}$	
I .	$\frac{\Delta I}{I}$.	I .	$\frac{\Delta I}{I}$.
48950	·0215	19610	·0197
19680	·0163	9819	·0184
9844	·0158	4920	·0163
4912	·0180	1965	·0179
1967	·0169	982	·0188
983	·0172	490	·0197
490	·0206	196	·0222
196	·0224	97·6	·0250
97·1	·0300	48·7	·0258
48·1	·0391	19·4	·0306
19·1	·0465	9·64	·0375
9·35	·0701	4·76	·0513
4·54	·101	1·87	·0701
1·66	·207	0·920	·0874
·742	·347	0·454	·100
·312	·603	0·178	·124
		0·0866	·154
		0·0408	·224
		0·0150	·336
		0·00729	·372
		0·00339	·475

the upper. The difference between the physical intensities of the two patches was then determined by the relative rotations of the nicols, and taken as the value of the differential threshold ΔI . The upper half of the field was then increased by the numerical value of ΔI to give a new value of I , and the lower increased again until it became just perceptibly brighter. In this manner measurements were obtained throughout the whole range of intensities available for various monochromatic radiations and for white light, two series of which are reproduced in Table I. From an inspection of these data it will be seen that they are not connected by any linear relationship.

In a recent paper by Hecht *, data from various sources relating to the Weber and Fechner laws in vision have been discussed and the following conclusion reached :—

“There is presented a series of data, assembled from various sources, which proves that in the visual discrimination of intensity the threshold difference ΔI bears no constant relation to the intensity I . The evidence shows unequivocally that, as the intensity rises, the ratio $\frac{\Delta I}{I}$ first decreases and then increases.”

From the evidence available Parsons † also concludes : “Weber’s law does not hold good for very low or very high intensities of stimuli, and is only approximate at best.”

While König’s measurements are probably beyond criticism, the interpretation of them as a valid experimental examination of the Weber law appears to be unsound for the following reasons :—

In observing the patch of light, one-half being at an intensity I and the other at a greater intensity $I + \Delta I$, two sensations are evoked by the stimulation of two adjoining retinal areas, whereas the Weber law deals with but a single sensation at any one time.

It has been shown by Allen ‡ that stimulation of a retinal area elicits complex neural reactions which modify the sensitivity of adjoining areas. The magnitude of the inductive reactions varies in some way with the intensity and duration of stimulation and with the wave-length of the light employed. The unequal stimulation of two adjoining areas by the same hues but of different intensities, as in König’s experiments, causes mutual inductive actions which tend to equalize the sensations. Under such conditions a value of ΔI obtained by slowly increasing the brightness of one patch cannot accurately represent the real differential threshold, and the ratio $\frac{\Delta I}{I}$ will

consequently be either too large or too small. It has been shown by Allen that the darkness adaptation of the unused eye further modifies the sensitivity of the receptors in the observing eye.

* Journ. Gen. Physiol. vii. p. 265 (1924).

† Loc. cit. p. 23.

‡ Journ. Op. Soc. Am. vii. pp. 583, 913 (1923); *ibid.* ix. p. 375 (1924); *ibid.* xiii. p. 383 (1926).

One of the outstanding features of the visual mechanism is its great amplitude of adaptation, or its ability to respond accurately to stimuli varying over a wide range of intensity. It might be expected, in order for the process of adaptation to operate in the most efficient manner, that there would occur some modifications of the neural reaction processes at different ranges of intensity of stimulation. König, however, seems to have taken no precautions against the danger of concealing such possible modifications.

Consider, for example, his curve obtained with radiation of wave-length 6700 Å. There are in it only 16 points, representing a very wide range of intensities from the least perceptible to the greatest. The extensive graphical interpolation necessitated by such widespread points would effectively conceal any alterations in the response of the receptors except those of the greatest magnitude. Such measurements, therefore, should not be interpreted as a satisfactory experimental examination of Weber's law.

Again, much work has been done with white light. It has been found by Allen * that each spectral wave-length is a physiological stimulus with a character peculiar to itself, differing, sometimes widely, from that possessed by every other hue. Since white light may be composed of all wave-lengths in the visible spectrum, and in varying amounts depending on the nature of the source, it would contain practically an infinite number of physical variables, and in consequence would elicit a corresponding complexity of sensations. In considering the interpretation of experimental results, it should be borne in mind that the essential condition of the scientific method of experimentation is the reduction to a minimum of the number of variables observed at any one time.

These criticisms of König's method may be briefly summarised thus :—

1. Owing to the nature of the apparatus, two distinct sensations of different intensities were obtained at the same time. This is not the condition required by Fechner's interpretation of Weber's ratio.

2. The normal condition of the sensitivity of the retina was not maintained because of the presence of inductive processes.

* Journ. Op. Soc. Am. xiii. p. 383 (1926).

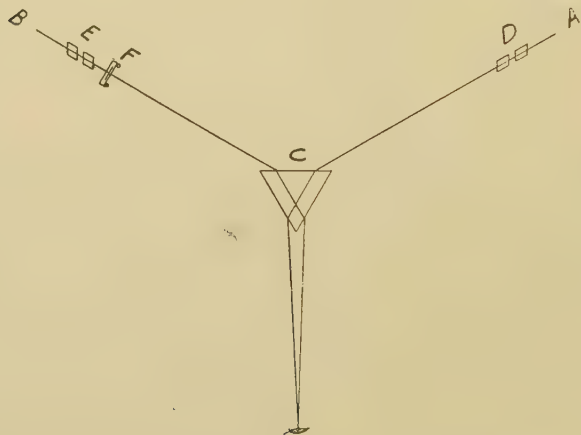
3. The method of adding the value of the differential threshold to the intensity in order to determine the next intensity at which to examine Weber's ratio, leaves a constantly widening gap between successive readings far too great for an exacting examination of the law.

4. The use of white light in examining simple visual laws introduces a confusing complexity.

Experimental Arrangements for a New Examination of Weber's Law.

In the present attempt to examine Weber's law and to avoid the criticisms of König's method, the arrangement of apparatus was similar in principle to the diagram in fig. 1.

Fig. 1.



Two incandescent lamps, A and B, operated from a 60-cycle alternating current of 110 volts, were the sources of radiation. The light was passed by two collimators through two refracting edges of the prism C in such a manner that radiations of the same wave-length from each source were superposed in the focal plane of the Hilger shutter eyepiece of the telescope. The actual instrument used was the tricolour spectrometer designed by Professor Frank Allen*. The intensity of the radiation from each source was controlled by pairs of nicol prisms, D and E, placed between the sources and the slits of the collimators.

* Journ. Op. Soc. Am. viii, p. 339 (1924).

Between the source B, the corresponding nicol prisms E, and the prism C was placed in the path of the light a camera shutter F, which was normally kept closed. By this arrangement a small patch of light of the desired wavelength of constant and measured intensity could be observed, and a measured increment of the same colour could be added uniformly over the whole of the same patch by opening the camera shutter for a brief interval of time. Thus by repeated trials the just perceptible increment could be determined with precision, and without employing a second patch of colour as a standard of comparison.

The apparatus was mounted in a room well lighted by diffused daylight, both eyes being thus adapted to the state in which they are ordinarily used. A definite intensity I of the stimulus from the source A was obtained by rotating the polarizer of the nicols D. This stimulus was received on the right eye for approximately 2 seconds when the camera shutter was opened. An increase of intensity was looked for, since the release of the shutter allowed an increment of radiation of intensity ΔI , coming from the source B, to be superposed on the intensity I for a period of one-fifth of a second. A rest interval of 3 minutes was then allowed for the eye to resume its normal condition, after which the process was repeated, the value of the intensity ΔI being either raised or lowered according to whether it had been noticeable or not at the previous opening of the shutter.

When the intensity had been reached at which the increment was just perceptible, its magnitude was determined by measuring the angle between the principal planes of the nicols E, the magnitude of the intensity I being likewise determined from the other pair of nicols D. No attempt was made to determine the absolute value of the Weber ratio $\frac{\Delta I}{I}$.

Examination of Weber's law with three different spectral colours—red, yellow, and green—of wave-lengths 6678 Å., 5875 Å., 5015 Å., was made in this manner.

The measurements are given in Table II. The intensity of the stimulus is proportional to $\sin^2 \phi$, where ϕ is the angle between the principal planes of the nicols A, such that where $\phi = 0$ the nicols transmit no light. Similarly,

$\sin^2 \theta$ determines the intensity of the differential threshold, θ being the angle between the principal planes of the nicols B. No numerical relation between the intensity and the differential thresholds was determined.

The data are shown graphically in figs. 2, 3, and 4, where stimulating intensities are plotted as abscissæ and

TABLE II.

Experimental Confirmation of Weber's Law.

Intensity = $\sin^2 \phi$. Differential threshold = $\sin^2 \theta$.

CURVE A. $\lambda = 6678 \text{ \AA.}$		CURVE B. $\lambda = 5875 \text{ \AA.}$		CURVE C. $\lambda = 5015 \text{ \AA.}$	
$\sin^2 \phi$.	$\sin^2 \theta$.	$\sin^2 \phi$.	$\sin^2 \theta$.	$\sin^2 \phi$.	$\sin^2 \theta$.
1.0000	0.3167	1.0000	0.1141	1.0000	0.4318
0.9700	0.3059	0.9700	0.1068	0.9700	0.4088
0.8830	0.2742	0.8830	0.0862	0.8830	0.3580
0.7550	0.2240	0.8078	0.0677	0.7550	0.2820
0.7114	0.2073	0.7550	0.0620	0.7035	0.2563
0.6712	0.1979	0.5867	0.0499	0.6545	0.2412
0.6292	0.1887	0.4134	0.0347	0.5867	0.2252
0.5867	0.1796	0.2500	0.0205	0.4134	0.1796
0.4134	0.1372	0.1170	0.0055	0.2500	0.1294
0.2500	0.0997	0.0300	0.0007	0.1786	0.1104
0.2132	0.0896			0.1170	0.0912
0.1786	0.0814			0.0669	0.0606
0.1590	0.0751			0.0300	0.0380
0.1464	0.0691				
0.1313	0.0606				
0.1170	0.0513				
0.1006	0.0403				
0.0904	0.0369				
0.0688	0.0288				
0.0467	0.0231				
0.0301	0.0181				
0.0076	0.0116				

the corresponding differential thresholds as ordinates. It will be seen that the curves obtained are all exact straight lines, there being, however, at definite values of the intensities abrupt changes in the slope similar to those obtained by Allen in his detailed experimental study of the Ferry-Porter law.

Each part of the graph, therefore, conforms to the law

$$\frac{\Delta I}{I} = C,$$

where the constant C has a different value for each part of the graph.

Fig. 2.

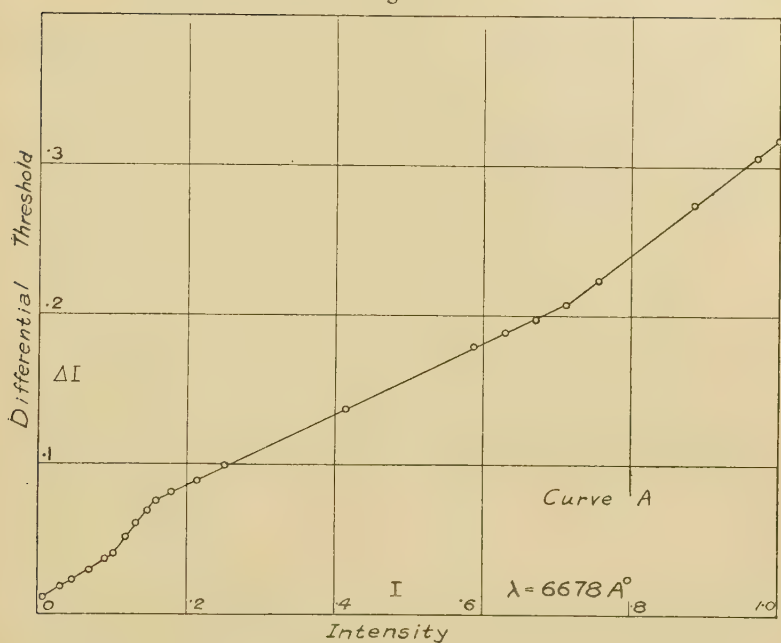
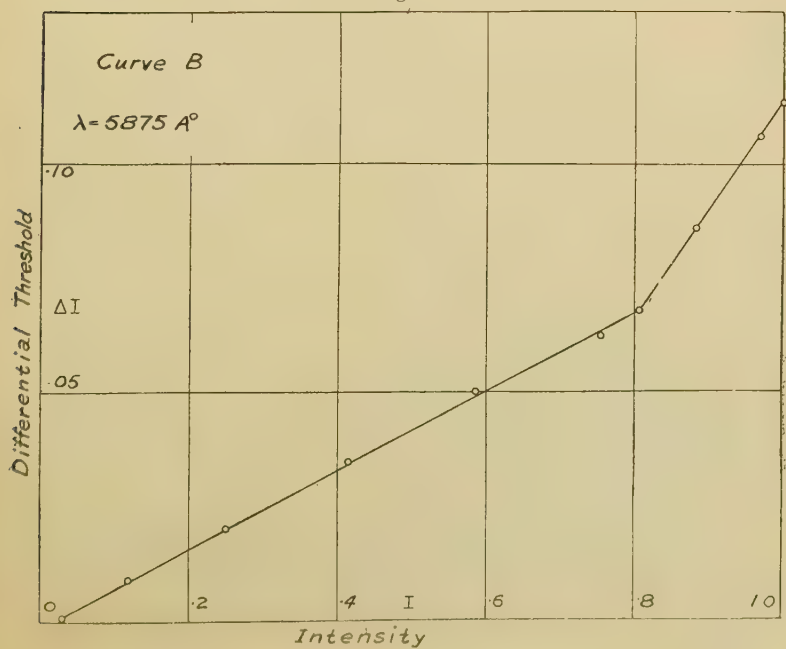
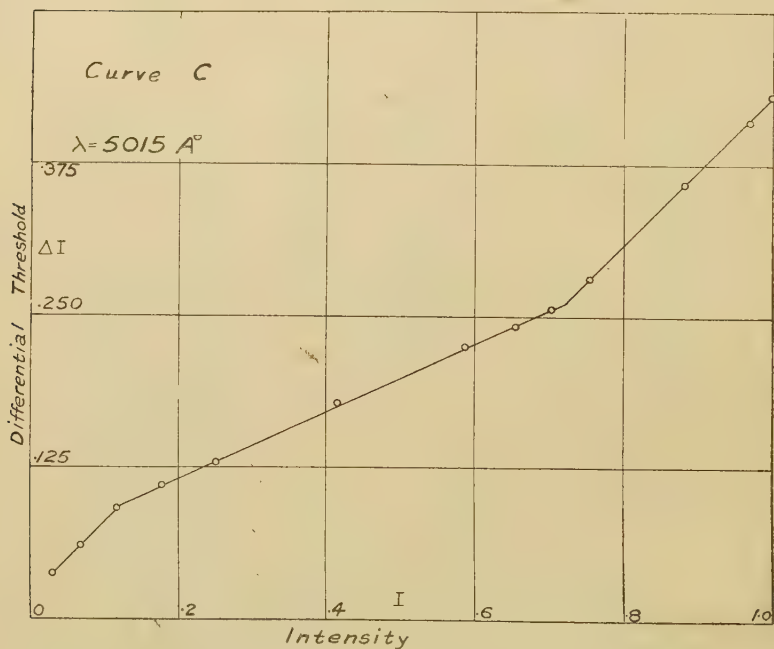


Fig. 3.



It is evident from the curves presented in this communication that for the visual sense Weber's law holds exactly over all ranges of intensity, there being, however, at definite intensities sudden changes in the value of the ratio of the differential threshold to the stimulating intensity. Previous investigators had been expecting to obtain a single constant holding for all ranges of intensity, and their failure to recognize the possibility of different

Fig. 4.



constants for different ranges of intensity has led to the conclusion that Weber's law was not true. The different numerical values for the ratio obtained by various observers would be accounted for both on this basis and on an observation which we have made that the ratio varies with the area of the surface examined.

A more detailed discussion of the results will be deferred to later parts of this communication in which experiments on other senses will be described.

In conclusion the authors desire to emphasize the fact that the purpose of this paper is to show that a definite algebraic ratio connecting the increment of intensity with the intensity of the stimulus does exist. It is not intended to be a complete quantitative investigation of the subject, for the laboratory facilities were not sufficiently extensive to permit the absolute values of the stimuli to be readily determined. Indeed, it would seem better to defer such measurements until a more detailed examination of the conditions underlying the law has been made.

We desire to express our sincere thanks to Professor Frank Allen, not only for the use of his laboratory, but for much stimulating criticism during the progress of the work. We also desire to thank the Hudson's Bay Company and the National Research Council of Canada for the substantial grants which enabled this work to be undertaken.

LXXV. *The Psychophysical Law.*—II. *The Sense of Audition.* By P. A. MACDONALD, M.Sc., Hudson Bay Fellow, and JOHN F. ALLEN, B.A., Research Assistant, University of Manitoba, Winnipeg, Canada*.

IN subjecting Weber's Law to an examination in the sense of hearing, the fundamental principle and precautions followed were similar to those employed in the investigation of the same law in vision which was described in a previous communication † to this Magazine.

The source of sound of adjustable intensity and frequency was a Stern tonvariator which was sounded by a stream of air previously collected over water in a constant-pressure tank. The particular instrument first used was that formerly employed by Miss Weinberg and Professor Allen in their researches on the critical frequency of pulsation of tones ‡. The frequency chosen by the present writers was 180 D.V., which was within the limits of frequency studied by the former investigators. The intensities used in this part of the present communication were

* Communicated by Prof. Frank Allen.

† Macdonald and J. F. Allen, "The Psychophysical Law.—I. Vision," see Part I. of this paper, p. 817.

‡ Phil. Mag. xlvii. pp. 50, 941 (1924).

selected to conform to those which had been assumed, as stated by other investigators *, to be proportional to the blowing pressure of the air. The weights placed on the pressure tank were therefore taken as proportional to the intensities of the sound emitted by the tonvariator. Considering the small range of intensities employed, this assumption is probably quite accurately justified.

TABLE I.

Weber's Law in Audition. Frequency 180 D.V.

I.	Log I.	$\Delta I.$	$\frac{1}{\Delta I}.$
Kilograms.		Kilogram.	
0.5	1.699	0.1575	6.349
1.0	0	0.1825	5.479
1.5	0.176	0.1975	5.063
2.0	0.301	0.2075	4.817
2.0	0.301	0.2070	4.831
3.0	0.477	0.2220	4.505
3.5	0.544	0.2275	4.396
1	0	0.182	5.495
3	0.477	0.222	4.505
5	0.699	0.247	4.049
7	0.845	0.267	3.745
9	0.954	0.287	3.484
11	1.041	0.297	3.367
2	0.301	0.212	4.717
4	0.602	0.237	4.219
6	0.778	0.257	3.891
8	0.903	0.277	3.610
10	1.000	0.292	3.425
12	1.079	0.302	3.311

A, readings taken Sept. 14th A.M.

B, " " " " " P.M.

C, " " " " " 15th A.M.

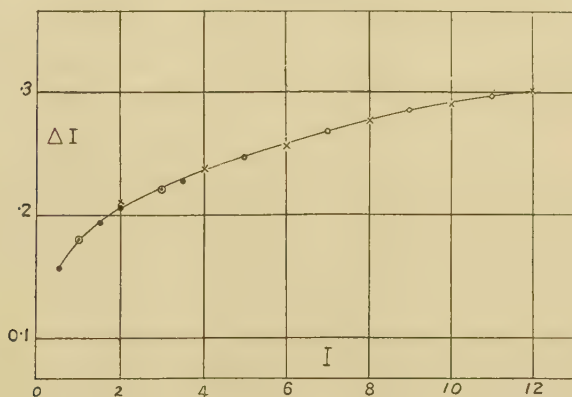
The experimental procedure was as follows:—After listening to the sound for 2 seconds, a small additional weight was lowered to the top of the tank by a lever so as to increase suddenly the intensity of the sound. By repeated trials a value of this weight was found which produced a just perceptible increment of intensity. In this manner a series of measurements was made, covering the selected range of intensities, which are given in Table I.

* Love and Dawson, Phys. Rev. xiv. p. 49 (1919).

The values in this table are arranged in three groups, which were obtained, as indicated in the table, on three successive half-days. Several measurements of three intensities, it will be noticed, were found which agree extremely well.

In fig. 1, all the values of ΔI , the just perceptible increments or differential thresholds, are plotted as ordinates with corresponding values of the intensity I as abscissæ. The points fall on a single curve which is unmistakably concave towards the horizontal axis. It is quite evident that these measurements do not even remotely conform to Weber's law, which states that the

Fig. 1.



Weber's Law. The ratio of ΔI to I is not constant.

Group C in Table I. are denoted by solid circles.

„ B „ „ „ circles.

„ A „ „ „ „ 's.

ratio of ΔI to I is a constant. For, if they did, the graph should be a straight line. The curved form of the graph suggested that possibly a logarithmic relation might exist between ΔI and I , and consequently reciprocals of ΔI and values of $\log I$ were plotted in fig. 2 as ordinates and abscissæ respectively.

The resulting graph is evidently composed of two linear parts, the one to the left indicated, however, by only two points which represent the lowest intensities. The remaining points lie very close to the same straight line, though those marked with an \times , which represent group A of the measurements in Table I., may form a slightly

different straight line. The graph is represented by the equation

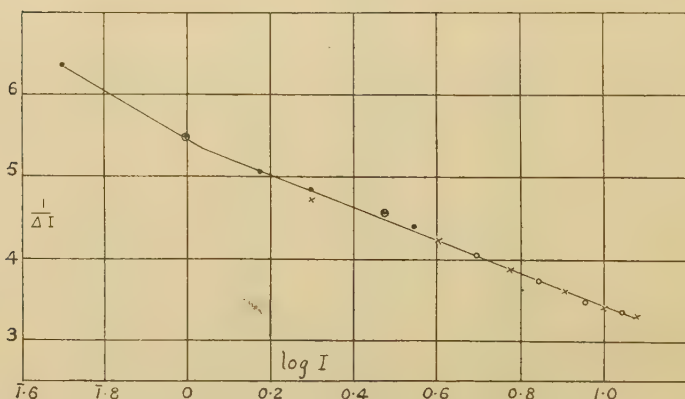
$$\frac{1}{\Delta I} = -k^2 \log I + C,$$

or, in analogy with Weber's law,

$$\frac{\frac{1}{\Delta I}}{\log I} = C_1,$$

where k^2 , C , and C_1 are constants whose numerical values differ for the two parts of the graph.

Fig 2.



Weber's Law. * The ratio of $\frac{1}{\Delta I}$ to $\log I$ is constant in each part of the graph.

Group C in Table I. are denoted by solid circles.

„ B „ „ „ circles.

„ A „ „ „ „ 'x's.

As some doubt was entertained whether it was justifiable to use the weights on the tank as measures of the intensity of the sound, it was decided to re-examine the relationship of the two intensities with another tonvariator of higher pitch and a greater range of intensities.

Since with different blowing pressures both the intensity and the frequency of the sound alter, it was necessary before using the instrument to calibrate both variables as functions of the blowing pressure. The two operations were carried out simultaneously by using a Rayleigh disk,

a device which has so frequently been employed that no description of it is necessary here.

The disk having been set approximately in resonance with another tonvariator at the frequency of 575 D.V. by adjusting the length of the resonance tube in which the disk was suspended, the room was vacated by the observer, who made further adjustments of the tonvariator from the adjoining room by a rod passing through a hole in the wall. In the observer's room was also placed the pressure tank, from which air was delivered to the tonvariator through a rubber tube. A definite blowing pressure was obtained by placing weights on the top of the tank, and the frequency of the tonvariator altered until the deflexion of the disk was a maximum. The tonvariator was then in exact resonance with the disk, the deflexion of which was a measure of the intensity I of the sound. The deflexion was read in centimetres by a telescope, and in no case was it greater than 10° .

The following procedure was adopted in making a series of measurements. A definite weight having been placed on the pressure tank, the tonvariator was adjusted to give the proper frequency, after which the sound was stopped to allow the restoration of the ear to its normal sensitivity. The observer then placed his head against a rest in order to keep it always in the same position for an observation, and, after allowing the tonvariator to sound for approximately 2 seconds, lowered by a cord a small weight to the top of the tank and listened for an increase in the intensity of the sound. Observing a rest period of 5 minutes between successive trials, the small weight was altered in magnitude until a value was found that caused a just perceptible increase in the intensity of the sound. The small weight was then taken as a measure of the magnitude of the differential threshold ΔI . The data obtained in this manner are given in Table II. and are shown graphically in fig. 3.

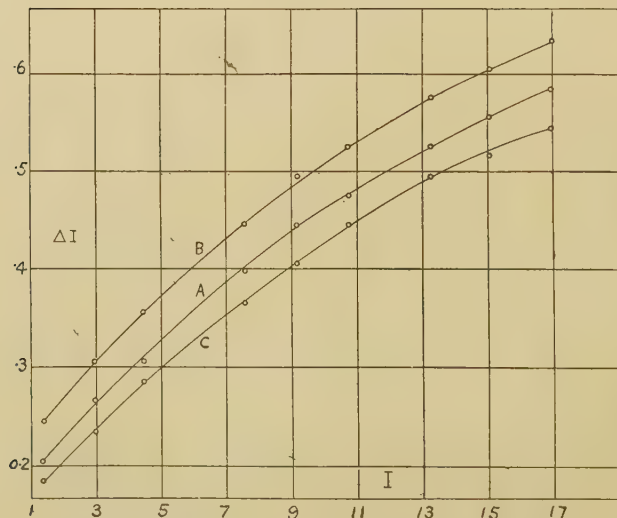
It will be noticed in the table that the values of the intensity I , given by deflexions of the Rayleigh disk, are not proportional to the weights in the first column. The graph for the calibration of the intensities of the sound in centimetres of deflexion when they are plotted against the weights on the tank is therefore not a straight but a curved line. In the measurements of increments, however, the additional weights placed on the pressure tank are used

TABLE II.

Weber's Law in Audition, for different States of Aural Adaptation. Frequency 575 D.V.

W.	I.	Log I.	Normal, A.		Depression, B.		Enhancement, C.	
			$\Delta I.$	$\frac{1}{\Delta I}.$	$\Delta I.$	$\frac{1}{\Delta I}.$	$\Delta I.$	$\frac{1}{\Delta I}.$
Kilo-grams.	Cm.		Kilo-gram.		Kilo-gram.		Kilo-gram.	
4	1.4	0.146	0.205	4.878	0.245	4.082	0.185	5.405
6	3.0	0.477	0.265	3.774	0.305	3.279	0.235	4.255
8	4.5	0.653	0.305	3.279	0.355	2.817	0.285	3.509
12	7.6	0.881	0.395	2.532	0.445	2.247	0.365	2.740
14	9.2	0.964	0.445	2.247	0.495	2.020	0.405	2.469
16	10.8	1.033	0.475	2.105	0.525	1.905	0.445	2.247
20	13.3	1.124	0.525	1.905	0.575	1.739	0.495	2.020
24	15.1	1.179	0.555	1.802	0.605	1.653	0.515	1.942
28	17.0	1.230	0.585	1.709	0.635	1.575	0.545	1.835

Fig. 3.



Weber's Law. The ratio of ΔI to I is not constant.

Graph A is for normal sensitivity of the ear.

„ B „ depressed „ „

„ C „ enhanced „ „

as values of ΔI , and their reciprocals are also employed for the ordinates of the graphs in both figures. This procedure does not involve any error either in the graphs themselves or in the law deduced from them, for we found that portions of the calibration curve may without appreciable error be taken as straight lines through an amount representing as much as one or even 2 kilograms. The additional weights necessary to obtain just perceptible increments of intensity varied from 0.185 to 0.635 kilogram, and are well inside the limits within which the calibration curve may be regarded as linear. Indeed, by this method increased precision of measurement is secured, for the additional deflexions of the disk by the increased weights would be only from about 0.16 to 0.3 cm., quantities so small that errors of observation would be relatively large, whereas the additional weights vary from 185 to 635 grams, in measuring which no error is involved.

In fig. 3 the values of ΔI and I are plotted as ordinates and abscissæ respectively, as in fig. 1, to see whether the linear relation expressed by Weber's law exists between them. This graph also clearly shows that the law is not true for the sense of hearing. On plotting in fig. 4 the reciprocals of the three sets of measurements of ΔI against the values of $\log I$, as in fig. 2, we obtain three graphs of unquestionably linear form, each of which consists of two parts represented by the above equations with appropriate values of the constants.

The three converging graphs represent the same number of different states of sensitivity or adaptation of the right ear of the observer, of which A is for normal, B for depressed, and C for enhanced sensitivity. The conditions under which they were obtained are described by one of the writers in the following paper in this number*.

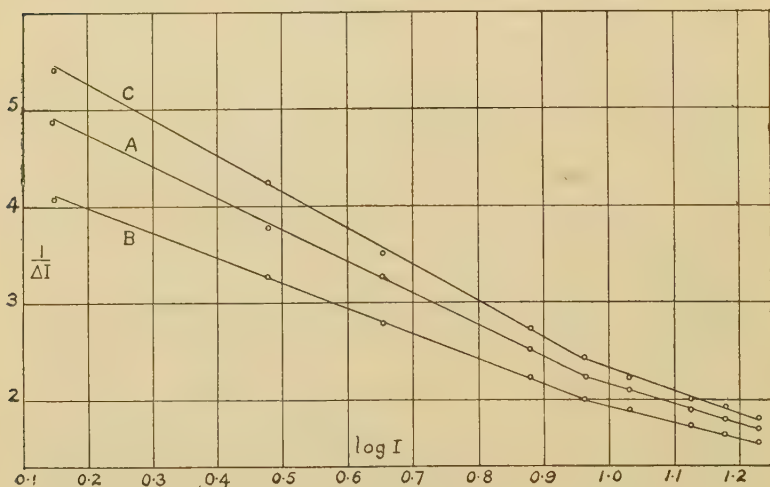
From this figure it is evident, in addition, that the new form of Weber's law for the sense of hearing applies not only to the normal state of sensitivity of the aural receptors, but to the two conditions of adaptation, depression and enhancement as well.

Owing to the importance of Weber's law and its numerous applications, arrangements are now being made

* John F. Allen, "The Depression and Enhancement of Auditory Sensitivity," p. 834, *infra*.

to continue the investigation with experimental arrangements that will afford a much greater range of intensities, both high and low, than has been possible with the tonvariators.

Fig. 4.



Weber's Law. The ratio of $\frac{1}{\Delta I}$ to $\log I$ is constant in each part.

Graph A is for normal sensitivity of the ear.

„ B „ depressed „ „
 „ C „ enhanced „ „

LXXVI. *The Depression and Enhancement of Auditory Sensitivity.* By JOHN F. ALLEN, B.A., *Research Assistant in Physics, University of Manitoba, Winnipeg* *.

THE investigations conducted by Prof. Frank Allen and his associates on the senses of vision †, touch ‡, taste §, temperature and pain ||, the contraction of muscles ¶,

* Communicated by Prof. Frank Allen.

† Allen, *Journ. Op. Soc. Am.* vii. pp. 583, 913 (1923); *ibid.* ix. p. 375 (1924); *ibid.* xiii. p. 383 (1926).

‡ Allen and Hollenberg, *Quart. Journ. Exper. Physiol.* xiv. p. 351 (1924). Allen and Weinberg, *ibid.* xv. p. 377 (1925).

§ Allen and Weinberg, *ibid.* p. 385 (1925).

|| Allen and Macdonald, *ibid.* xvi. p. 321 (1927).

¶ Allen and O'Donoghue, *ibid.* xviii. p. 199 (1927).

and the secretion of glands * have uniformly shown that depression and enhancement of sensitivity or response of the organs are produced as two of the results of stimulation, the amount and character varying with the intensity of the stimulus and the conditions under which it is applied. Very weak stimulation of α intensity, as it has been termed, depresses the sensitivity of the retina, while more intense stimulation of β , γ , etc. intensities enhances it. In the sense of taste the actions of weak and strong gustatory stimuli are similar to those in vision. In the sense of touch, and probably in that of hearing, the reverse is true, since weak tactile stimuli enhance and strong depress the sensitivity. All these induced effects, which are variously due to motor, secretory, or sensory reflex action, occur with both ipsilateral and contralateral stimulation. It has also been discovered that when the sensitivity of receptors, muscles, and glands has been disturbed by stimulation, their normal condition is restored by a series of neural oscillations of depression and enhancement—that is, of the corresponding physiological processes of inhibition and facilitation, during which the response is diminished or augmented respectively, according to the phase of the oscillation which is predominant when subsequent stimulation occurs.

In studying auditory responses by the method of the critical frequency of pulsation or flutter of tones, Miss Weinberg and Allen † did not obtain enhanced sensitivity of the receptors, though depression was found to occur. At that time the oscillatory character of the recovery of normal sensitivity had not been recognised, and consequently they were not aware of the very simple method of obtaining the anticipated enhancement which is employed in the present investigation.

This new method was developed by Macdonald and the writer ‡ for the purpose of testing the validity of Weber's law in the auditory sense, and is analogous to the method employed by them for a similar purpose in vision §.

The source of sound was a Stern tonvariator blown by air from a constant-pressure tank. The tonvariator was

* Allen, *ibid.* xix. pp. 337, 363 (1929).

† Phil. Mag. (6) xlvii. pp. 50, 126, 141, and 941 (1924).

‡ Macdonald and J. F. Allen, "The Psychophysical Law.—II. Audition," Phil. Mag. ix. p. 827 (1930).

§ Macdonald and J. F. Allen, "The Psychophysical Law.—I. Vision," Phil. Mag. ix. p. 817 (1930).

always adjusted to give a pure tone of frequency 575 D.V., the intensity of which was measured by the deflexions of a Rayleigh disk. The tonvariator and disk were conveniently placed in a room by themselves, and the pressure tank and observer were in a room adjoining. Through a hole in the brick wall the sound came to the observer, while by means of a telescope the scale of the disk apparatus was read, and the tonvariator maintained in adjustment by a long rod.

In order to obtain depression and enhancement of sensitivity of the auditory receptors, a second tonvariator was placed in the same room with the observer. This was adjusted to the same frequency, 575 D.V., as the tonvariator with which the measurements were made.

The Normal Graph.

The first measurements made were for the purpose of obtaining a graph for the normal sensitivity of the ear which should form the standard with which other graphs for different conditions of sensitivity could be compared. The method of obtaining the normal graph was described in the paper by Macdonald and Allen to which reference has been made. Briefly, it consists of a series of measurements for the whole range of intensities within the capacity of the tonvariator, each of which represents the increment of sound which, when added to the intensity of the tone previously emitted by the tonvariator, is just perceptible. The measurements of the series of just perceptible normal increments, or differential thresholds, are given in Table I., and are plotted as graph A in fig. 1, with values of the logarithms of the intensity as abscissæ and reciprocals of increments as ordinates. The graph consists of two linear parts with an abrupt change of slope, each of which conforms to the equation :

$$\frac{1}{\Delta I} = -k^2 \log I + C,$$

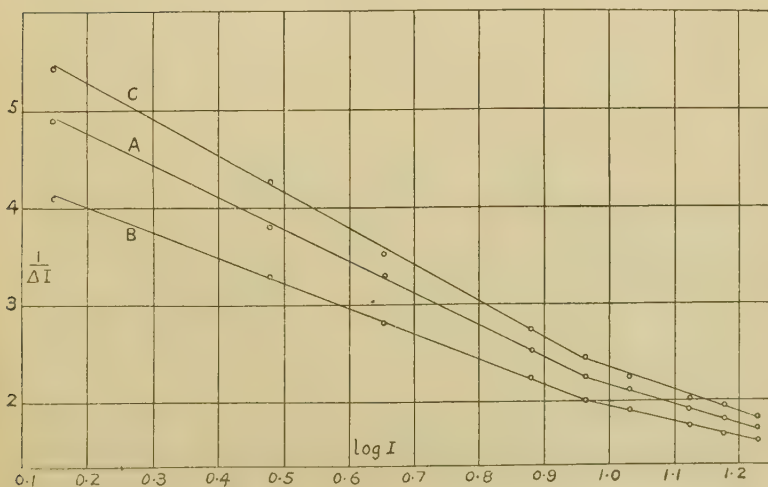
where I is the intensity of the tone, or the deflexion in centimetres of the Rayleigh disk which is proportional to it; ΔI is the just perceptible increment of intensity, or the additional weight in kilograms placed upon the tank to give the increased intensity; and k^2 and C are constants. The negative sign indicates the direction of the slope.

TABLE I.

Enhancement and Depression of Auditory Sensitivity.
Ipsilateral Stimulation. Frequency 575 D.V.

W.	I.	Log I.	Normal, A.		Depression, B.		Enhancement, C.	
			$\Delta I.$	$\frac{1}{\Delta I}.$	$\Delta I.$	$\frac{1}{\Delta I}.$	$\Delta I.$	$\frac{1}{\Delta I}.$
Kilo-grams.	Cm.		Kilo-gram.		Kilo-gram.		Kilo-gram.	
4	1.4	0.146	0.205	4.878	0.245	4.082	0.185	5.405
6	3.0	0.477	0.265	3.774	0.305	3.279	0.235	4.255
8	4.5	0.653	0.305	3.279	0.355	2.817	0.285	3.509
12	7.6	0.881	0.395	2.532	0.445	2.247	0.365	2.740
14	9.2	0.964	0.445	2.247	0.495	2.020	0.405	2.469
16	10.8	1.033	0.475	2.105	0.525	1.905	0.445	2.247
20	13.3	1.124	0.525	1.905	0.575	1.739	0.495	2.020
24	15.1	1.179	0.555	1.802	0.605	1.653	0.515	1.942
82	17.0	1.230	0.585	1.709	0.635	1.575	0.545	1.835

Fig. 1.



Enhancement and depression of auditory sensitivity with
ipsilateral stimulation.

A, normal sensitivity; B, depressed sensitivity; C, enhanced sensitivity.

It will be noticed in the tables, as remarked in a former paper on Weber's law to which reference has been made, that the values of the intensity I , given by deflexions of the Rayleigh disk, are not proportional to the weights in the first column. The graph for the calibration of the intensities of the sound in centimetres of deflexion when they are plotted against the weights on the tank is therefore not a straight but a curved line. In the measurements of increments of intensity, however, the additional weights placed on the pressure tank are used as values of ΔI , and their reciprocals are also employed for the ordinates of the graphs in both figures. This procedure does not involve any error either in the graphs themselves or in the law deduced from them, for we found that portions of the calibration curve may without appreciable error be taken as straight lines through an amount representing as much as 1 or even 2 kilograms. The additional weights necessary to obtain just perceptible increments of intensity varied from 0.185 to 0.635 kilogram, and are well inside the limits within which the calibration curve may be regarded as linear. Indeed, by this method increased precision of measurement is secured, for the additional deflexions of the disk by the increased weights would be only from about 0.16 to 0.3 cm., quantities so small that errors of observation would be relatively large, whereas the additional weights vary from 185 to 635 grams, in measuring which no error is introduced.

The Effect of Ipsilateral Stimulation.

In order to study the effect of ipsilateral stimulation, the second tonvariator mentioned above was placed close to the right ear of the observer and tuned to exactly the same pitch as that of the measuring tonvariator. The intensity of the sound emitted by the stimulating tonvariator was not determined, but it was probably fifteen or twenty times as great as that of the measuring instrument.

The experimental procedure was as follows:—First, the head was placed in the head-rest and the stimulating tonvariator sounded for 1 minute. It was then silenced and an increment reading taken immediately with the measuring tonvariator. It was found that a greater increment of sound-intensity than that which was formerly sufficient had to be added before it was distinguishable.

After resting for 10 minutes, without additional stimulation, another reading was taken, when it was found that a smaller increment than the normal amount could be distinguished. A sufficient time was then allowed for the ear to recover its normal state of sensitivity, when the readings were repeated with a higher intensity.

The complete series of measurements are given in Table I., and are plotted with the normal graph in fig. 1. Graph A represents the measurements of just perceptible increments when the ear is in its normal condition of sensitivity; B represents similar measurements when the ear is depressed in sensitivity; and C the corresponding measurements when the aural sensitivity is enhanced. Each graph consists of two linear parts, which are represented by the equation given above with appropriate changes in the values of the constants.

These measurements show that immediately following somewhat intense stimulation the auditory receptors are depressed in sensitivity. The enhancing neural process then gradually rises in influence, by means of which the receptors recover their normal sensitivity. The process does not then cease, but continues its action until the sensitivity becomes much enhanced. The inhibitory process then in turn rises to predominance, during which the receptors become depressed in sensitivity. In illustration of this oscillatory character of the neural reactions, it was found that, starting with normal equilibrium, the receptor sensitivity immediately after stimulation was depressed; in 7 minutes a normal reading was obtained, which indicated the restoration of the normal state; in 10 minutes the reading showed enhancement of sensitivity as indicated in fig. 1; finally, in 15 minutes, a normal measurement was again obtained. No further readings were taken to discover whether the oscillatory process subsided at this time or again depressed the sensitivity.

It is thus clear that in the auditory sense, as in other sensory, motor, and secretory processes, equilibrium is restored by a series of neural oscillations of a pendular type with a definite amplitude and periodic time, by means of which the receptor sensitivity becomes alternately depressed and enhanced. Possibly this behaviour of the nervous system may throw some light on the physiological nature of the processes of inhibition and facilitation which are still involved in deep obscurity.

The Effect of Contralateral Stimulation.

Having obtained depression and enhancement of sensitivity by stimulating the right ear, contralateral effects were sought by placing the stimulation tonvariator, with the same frequency and intensity as before, close to the left ear while the right was temporarily protected by a heavy pad of wool and metal. The left ear was then stimulated for the same time, 1 minute, as before, after which the right ear was uncovered and an increment reading taken with it. This measurement showed depres-

TABLE II.

Enhancement and Depression of Auditory Sensitivity.
Contralateral Stimulation. Frequency 575 D.V.

W.	I.	Log I.	Normal, A.		Depression, B.		Enhancement, C.	
			$\Delta I.$	$\frac{1}{\Delta I.}$	$\Delta I.$	$\frac{1}{\Delta I.}$	$\Delta I.$	$\frac{1}{\Delta I.}$
Kilo-grams.	Cm.		Kilo-gram.		Kilo-gram.		Kilo-gram.	
4	1.4	0.146	0.205	4.878	0.225	4.444	0.195	5.128
6	3.0	0.477	0.265	3.774	0.285	3.509	0.245	4.082
8	4.5	0.653	0.305	3.279	0.335	2.985	0.295	3.390
12	7.6	0.881	0.395	2.532	0.425	2.353	0.375	2.667
14	9.2	0.964	0.445	2.247	0.475	2.105	0.425	2.353
16	10.8	1.033	0.475	2.105	0.505	1.980	0.455	2.198
20	13.3	1.124	0.525	1.905	0.545	1.835	0.505	1.980
24	15.1	1.179	0.555	1.802	0.585	1.709	0.535	1.869
28	17.0	1.230	0.585	1.709	0.615	1.626	0.565	1.770

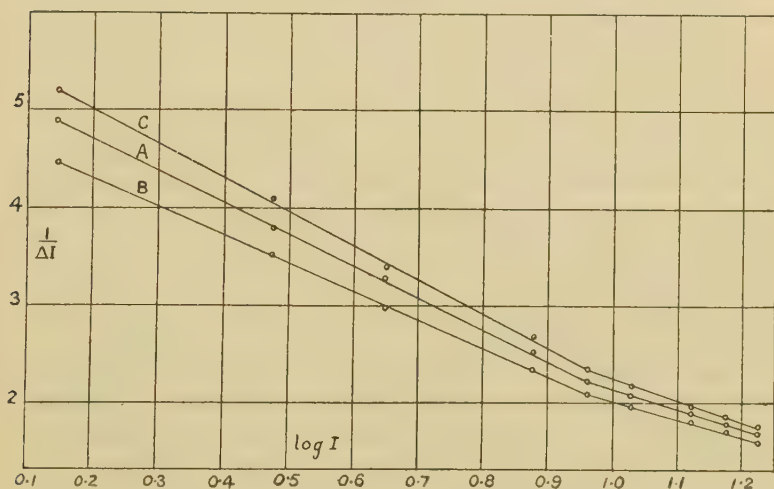
sion of sensitivity as before, but not in so marked a degree. After resting for 10 minutes a second reading was taken which showed enhancement of sensitivity, but also to a less extent than before. The measurements were similarly continued throughout the complete range of intensities. The results are plotted in fig. 2, from the data in Table II. in comparison with the same normal as before. In this figure A is the normal graph, B the graph for contralateral depression of sensitivity, and C that for contralateral enhancement. In both figures the depression graphs are below the normal and the enhancement above, since the reciprocals of increments are plotted as ordinates. The

contralateral effects are similar to the ipsilateral, except in magnitude. The linear parts of the graphs conform to the same equations as before, with suitable changes in the values of the constants.

Both groups of graphs in figs. 1 and 2 may also be represented by the equation :

$$\frac{1}{\log I} \frac{\Delta I}{I} = C,$$

Fig. 2.



Enhancement and depression of auditory sensitivity with contralateral stimulation.

A, normal sensitivity ; B, depressed sensitivity ; C, enhanced sensitivity.

which has been found by Macdonald and the writer* to denote the relationship between the just perceptible increment of intensity of a sound and the intensity, instead of Weber's law, which does not hold in the sense of hearing. The new law is thus verified in normal, depressed, and enhanced states of aural sensitivity under both ipsilateral and contralateral conditions of stimulation.

The marked convergence of both groups of graphs towards the greater values of the intensities, indicates that with high degrees of stimulation there will be no

* "The Psychophysical Law.—II. Audition," *Phil. Mag.* ix. p. 827 (1930).

distinction between the normal, depressed, and enhanced states, since all will become merged into one.

From these investigations it is clear that the auditory sense is subject to the same conditions and exhibits the same neural characteristics as the other senses, the muscles, and the glands. It is evident also that the afferent and efferent nerves of both ears are interconnected in the auditory centres of the cortex, where the same processes of inhibition and facilitation are elicited as, for example, in the senses of vision and taste. Possibly by their means, phenomena of binaural contrast may occur analogous to those in vision and taste. It may also be the case that contralateral influences may be involved in the process of locating the direction of sound.

It is quite probable, by analogy with the sense of touch, that enhancement of sensitivity instead of depression may first be evoked by very weak stimulation of the ear, and the oscillations thus be reversed in phase. It did not occur to the writer to test this supposition at the time the apparatus was available, and its study must be left for subsequent investigation.

I desire to express my thanks to Professor Frank Allen and Mr. P. A. Macdonald, M.Sc., for many suggestions in regard to these investigations; and also to the National Research Council of Canada for the grant by which I was enabled to act as Research Assistant to Professor Allen for the year.

LXXVII. *Concerning Electrical and other Dimensions.* By
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in the University of Reading*.

SUMMARY.

COMMON misconceptions concerning dimensions, which are specially noticeable where electrical and magnetic quantities are concerned, are discussed. The meaning of fractional indices in dimensional formulæ is considered, and a law is suggested for the frequency-distribution of the indices.

* Communicated by the Author.

I. *Certain Misconceptions.*

THE first part of this paper is an attempt to point out certain common misconceptions, which are chiefly noticeable when the dimensions of electrical and magnetic quantities are discussed. I believe my treatment is in essential agreement with work of Maxwell, J. J. Thomson, and P. W. Bridgman, but to a lesser extent with writings of J. H. Jeans, R. T. Birge, G. W. C. Kaye and T. H. Laby, W. Watson, and others.

The difficulties may be indicated by a few quotations. Thus, Kaye and Laby state* “ v , the ratio of the electromagnetic to the electrostatic unit of quantity . . . is a pure number.” But J. J. Thomson† and A. Gray‡ state the ratio of the units, v , in “cm. per second.”

Again, W. Watson states § :

$$[K^{-\frac{1}{2}}\mu^{-\frac{1}{2}}] = [LT^{-1}],$$

but later says “indicating this velocity of v , we have

$$[\mu^{-\frac{1}{2}}K^{-\frac{1}{2}}]/[LT^{-1}] = v.”$$

(This is typical of statements in many text-books.)

Further, I may quote R. T. Birge || :—“These difficulties are connected with the unknown dimensions of magnetic permeability μ , and specific inductive capacity ϵ In the present paper we are concerned only with numerical magnitudes and no particular attention has accordingly been paid to this matter of dimensions. . . . In a number of the equations given in Table c, the two sides of the equation do *not* check dimensionally unless one assumes μ and ϵ to be dimensionless.”

These difficulties disappear if we follow Maxwell, J. J. Thomson, and P. W. Bridgman. Thus Maxwell states ¶ :—“The only systems of any scientific value are the electrostatic and the electromagnetic systems. . . .

$$[e] = [L^{3/2}M^{1/2}T^{-1}]$$

in the electrostatic system.”

Again, J. J. Thomson writes **:—“On the electrostatic system of units K is of no dimensions . . .”

* ‘Phys. and Chem. Constants,’ 4th ed. p. 7 (1921).

† ‘Elements of Elec. and Mag.’ 4th ed. p. 479 (1909).

‡ ‘Abs. Measurements in Elec. and Mag.’ 2nd ed. p. 688 (1921).

§ ‘Text-Book of Physics,’ 7th ed. p. 788 (1920).

|| Phys. Rev., Suppl., i. no. 1, p. 66 (July 1929).

¶ ‘Elec. and Mag.’ 3rd ed. ii. p. 266 (1892).

** *Loc. cit.* p. 465.

On the ordinary electrostatic system the dielectric constant of a vacuum is by definition unity; a dielectric constant is measured as a ratio of two forces (or of two charges) expressed in the same units and is of no dimensions, just as are angles in radians and refractive indices. A similar argument applies to the electromagnetic system. The dimensions of charge, etc., as measured in the two systems will differ, and the ratio of the units will have the same dimensions as a velocity.

Objections to the above procedure must be on the grounds either that it is inexpedient or that it is incorrect. As regards expediency, we have the statement of Maxwell quoted above, and Bridgman's opinion, given in his 'Dimensional Analysis,' that no useful purpose has been served by retention of the symbols $[k]$ and $[\mu]$. We may also note that in the cases of angles and refractive indices no independent arbitrary units are preserved and used, and very little use has been found for the corresponding special dimensional symbols. Finally, we quoted above certain difficulties and contradictions resulting from the partial or inaccurate uses of other systems of units and dimensions.

People who object to the above type of procedure as being incorrect seem to forget that the dimensions of a quantity (that is measured in derived units) are but an abbreviated statement of how the derived unit was defined, telling us how the magnitude of the derived unit will be changed when we change the size of the arbitrary primary units, but make no other changes. The dimensions are the result of our method of definition and not a unique property of the thing we desire to measure*.

Thus, Jeans† objects that if we defined the unit of mass by the gravitational equation

$$m \cdot f = m \cdot m' / r^2,$$

mass must not be said to have the dimensions $[L^3T^{-2}]$, as:—

“we know that mass is something entirely apart from length and time, except in so far as it is connected with them through the law of gravitation.”

But the statement $[M] = [L^3T^{-2}]$ does not tell us how mass is related to length and time, but how our proposed *unit* of mass will be affected by changes in the sizes of our length and time units.

I will try to explain this by other examples. In place of

* N. E. Dorsey, *Int. Crit. Tables*, i. pp. 18–19.

† ‘*Elec. and Mag.*’ 2nd ed. par. 18 (1911).

defining unit force in the usual way, it appears to me to be just as legitimate (though less convenient) to define it by the "gravitational attraction." We should then have

$$P = m \cdot m' / r^2, \quad P = m \cdot f / G, \quad \text{and} \quad [P] = [L^{-2} M^2].$$

We cannot deduce that force is or is not "entirely apart from" time.

It may be difficult to realize that (in terms of $[M]$, $[L]$, $[T]$), it is only as the result of *definitions* that volume has the dimensions $[L^3]$, velocity $[LT^{-1}]$, etc., so I will discuss the problem a little further. Whenever we measure a quantity in terms of units of a different kind, we make use of properties of Nature. Even the use of "cubic centimetres" implies the possibility of making cubes defined by the cm. length unit; and before we can measure a volume as the product of three lengths, we must assume that eight equal cubes can be fitted together to form one cube having double the length of side. (Presumably this can only be done exactly where there is no gravitational field*.) Similarly, we could use properties of Nature and measure lengths in "light-seconds," and the unit of volume could be taken as the space enclosed by the "spherical" wave-front of light that had travelled in a vacuum from a point source for one second. Following the usual practice of omitting to state the details of the method of definition when we write down the dimensions, the measurements would now be said to be in "sec." and "sec.³" respectively of dimensions $[T]$ and $[T^3]$. If we desire to retain as primary units the cm., gm., and sec., there is no necessity to use "light-seconds"; but for the derived unit of volume, that defined by the light wave would be a legitimate alternative to the "cubic centimetre."

Again, after the manner of measuring angles as the ratio of lengths, velocities could be measured as fractions of that of light in a vacuum. The actual measurements would result in the ratio of two times or lengths, and velocity would have no dimensions in terms of $[M]$, $[L]$, and $[T]$.

I cannot, therefore, agree with Watson's statement (*loc. cit.*) that "the dimensions of any physical quantity must be independent of the particular system of units adopted"; the dimensions of permeability which Birge (*loc. cit.*) terms "unknown" seem merely arbitrary; and the dimensions of charge (as given in my quotation from Maxwell) seem no more "apparent" (Jeans, *loc. cit.*, paragraph 588) than are the dimensions usually given for area, volume, force, etc.

* Eddington, 'Report on Relativity Theory of Gravitation,' p. 28.

II. *Fractional Indices in Dimensional Formulæ.*

Secondly, let us consider the fractional indices in the dimensional formulæ. Were an arbitrary unit of volume used, and the length unit derived from it, $[V]^{\frac{1}{3}}$ would be used in place of $[L]$, and $\frac{1}{3}$, $\frac{2}{3}$, etc., would appear as indices. Thus indices $\frac{1}{2}$, $\frac{2}{3}$ are not specially peculiar and merely correspond to our "measuring" electrical and magnetic quantities by the mechanical results of their interaction in pairs.

The likelihood of fractional indices occurring may be indicated by the following discussion (which may also have other uses). If no derived units were used, all the indices would be unity. When a small arbitrary number of arbitrary primary units replace the multiplicity of independent units, zero index is of little importance, only indicating that certain arbitrary units were not used in the particular measurement. Apart from the question of convenience, $[L]^3$ and $[V]$, $[L]$ and $[V]^{\frac{1}{3}}$, $[L]/[T]$ and $[T]/[L]$, $[M][L]^3$ and $[L]^3/[M]$ are equally likely. Thus a single index in a dimensional formula is equally likely to fall in any one of the ranges ($-\infty$ to -1), (-1 to 0), (0 to 1), and (1 to ∞). But only fairly simple integers or fractions are to be expected, as the number of separate measurements used together is generally small.

The Table below indicates the frequency with which the various indices occur in our ordinary measurements :—

Magnitude of index in dimensional formula.																		
4	$3\frac{1}{2}$	3	$2\frac{1}{2}$	2	$1\frac{1}{2}$	1	$\frac{1}{2}$	0	$-\frac{1}{2}$	-1	$-1\frac{1}{2}$	-2	$-2\frac{1}{2}$	-3	$-3\frac{1}{2}$	-4	-6	
Number of occurrences in 443 cases taken at random.																		
1	0	11	1	36	9	128	49	—	35	93	4	46	0	25	0	4	1	
122				113				$81\frac{1}{2}$				$126\frac{1}{2}$						

I find that the frequency-distribution of the squares of the indices is very similar to that found for "non-dimensional constants" (*e.g.* $4\pi/3$)*. This is illustrated in the following Table, derived from the previous Table :—

Range of value of (index) ² .								
(0 to $\frac{1}{2}$)	($\frac{1}{2}$ to 1)	(1 to 2)	(2 to 4)	(4 to 8)	(8 to 16)	(16 to 32)	(32 to ∞)	
Number found.								
84	$110\frac{1}{2}$	$110\frac{1}{2}$	54	42	$38\frac{1}{2}$	$2\frac{1}{2}$	1	

* Bond, Phil. Mag. vii. pp. 719-721 (April 1929).

Number according to suggested distribution law.

110·7	110·7	110·7	55·4	27·7	13·8	6·9	6·9
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Fractional number according to suggested distribution law.

$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{64}$
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Department of Physics,
University of Reading.
December 18, 1929.

LXXVIII. *The Soft X-rays of Manganese.*

By F. C. CHALKLIN, *Ph.D.*, *University of Sheffield* *.

EXPERIMENTS making use of the photo-electric method have shown that for each of the elements iron, cobalt, nickel, and copper there exists, in the soft X-ray region, a considerable number of critical potentials. To account for these Professor O. W. Richardson and the writer have suggested a scheme involving the assumption that the critical potentials are due to transitions from a number of initial levels to a Rydberg series of virtual levels†. The scheme works well for iron and fairly well for cobalt and nickel, but for copper there is a large number of discontinuities for which the scheme does not account. It is clearly of interest to examine the elements which are near to iron, cobalt, nickel, and copper in the periodic table, and to ascertain whether or not the suggested scheme accounts for the critical potentials obtained.

In the present series of experiments the critical potentials of manganese have been determined by two distinct variations of the photo-electric method. The first of these methods depended on a simultaneous comparison of the photo-electric current produced by the manganese radiations with that produced by the radiations from an anticathode of which the critical potentials were known (*e. g.*, carbon).

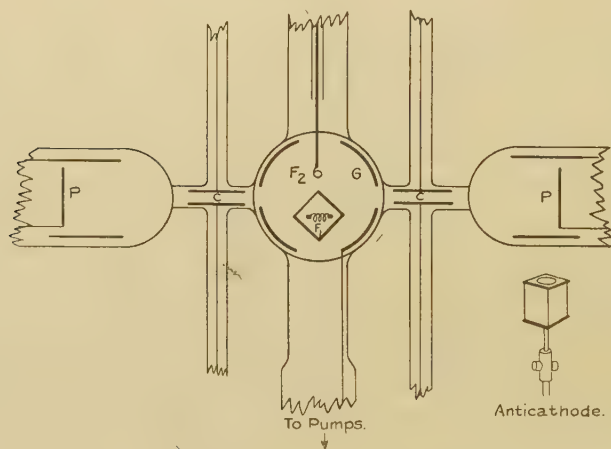
Fig. 1 shows the soft X-ray tube used for this purpose. The tube was constructed of transparent silica in order to facilitate the de-gassing process, and the seals were made

* Communicated by Prof. O. W. Richardson, F.R.S.

† Proc. Roy. Soc. A, **cxix.** p. 64 (1928); A, **cxxi.** p. 218 (1928).

with red sealing-wax. The electrodes were, with the exceptions mentioned below, all constructed of molybdenum*, in order to avoid as far as possible the danger of metal evaporating during the bake-out and condensing on the anticathode. The framework of the anticathode allowed four targets to be slid into position, thus surrounding a tungsten filament F_1^\dagger , from which an electronic stream could bombard the targets and de-gas them with little fear of the outer faces becoming sputtered. The targets were approximately 1.5 cm. wide and 2 cm. in height. The whole anticathode was mounted on an iron swivel, but was separated from it by a molybdenum rod, so

Fig. 1.



that the iron portions should not reach the high temperatures attained by the anticathode during bombardment. During these experiments a carbon target was exposed to one photo-electric cell, and the manganese target faced the other cell. Suitable potentials were applied to the condenser plates C and to the cylinder G to prevent ions and electrons from reaching the photo-electric plates P. A single tungsten filament F_2 supplied both targets with an electron stream. A Gaede three-stage mercury vapour

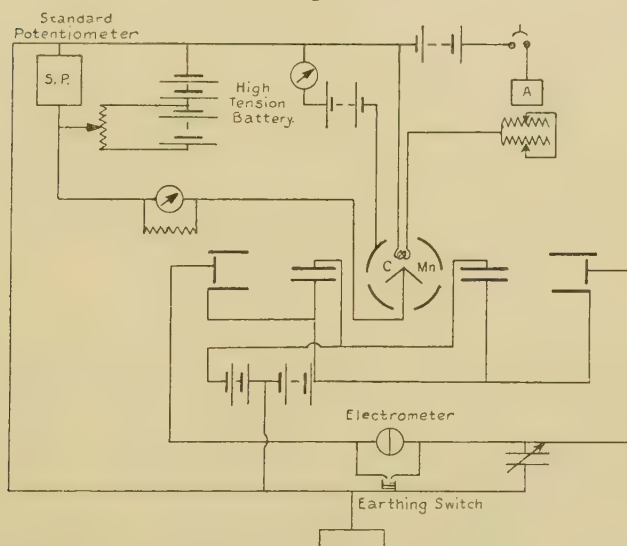
* Very kindly supplied by Metropolitan Vickers Electrical Co., Ltd., Manchester.

† For the tungsten wire used the writer is indebted to the General Electric Co., Ltd., Wembley.

pump was used to evacuate the apparatus, and, although a narrowing was necessary at a stopcock and at two liquid air traps, 3.5 cm. tubing was used where possible in order to facilitate the pumping.

Fig. 2 shows the electrical connexions in use during the experiment. Suppose the total thermionic current from filament to anticathode to be I_t . A fraction of it, Ai_t , goes to the carbon target and a fraction, Bi_t , goes to the manganese target. The photo-electric current due to each target may be taken as approximately proportional

Fig. 2.



to the electronic current bombarding that target. Again, it is well known that the photo-electric current is approximately proportional to the bombarding voltage V . Hence the photo-electric currents due to carbon and manganese are respectively $VMAi_t$ and $VNBi_t$, where M and N are constants representing the efficiency of each target in producing photo-electrons under the given conditions of geometry of tube and photo-electric plate. The ratio of the two photo-electric currents will be

$$\frac{i_{p2}}{i_{p1}} = \frac{NB}{MA} \quad \dots \dots \dots (1)$$

A and B are unlikely to vary very greatly with voltage (and certainly they should not vary discontinuously), so the ratio should remain constant as we vary the potential on the tube. However, at a critical potential of manganese, i_{p_2} will begin to differ from $VNBi_t$, and will only be represented by that expression again at some higher voltage. Hence, if the ratio were plotted against the voltage, it would be expected that the curve would in general be parallel to the voltage axis; it would begin to leave this straight line at a critical potential; the difference would increase to a maximum and the curve would then tend to return to the original course. The magnitude of the difference should be proportional to the thermionic current.

The two photo-electric plates were connected to opposite pairs of quadrants of a Dolezalek electrometer. One of these two insulated systems was made of variable capacity by placing, in parallel with it, a variable condenser. The variable condenser could then be adjusted until the electrometer did not charge up. When this is the case,

$$\frac{i_{p_1}}{C_1} = \frac{i_{p_2}}{C_2}, \quad \frac{i_{p_2}}{i_{p_1}} = \frac{NB}{MA} = \frac{C_2}{C_1} \dots \dots (2)$$

Since, in this experiment, we were only concerned with the critical potentials, it was not necessary to make an absolute determination of the ratio $\frac{i_{p_2}}{i_{p_1}}$ by the measurement of the capacities, C_1 and C_2 . After the variable condenser had been adjusted until the rate of charging up was very slow, the voltage was varied, and for each value of the voltage the rate of charging of the electrometer was observed. Discontinuities were found in the curves obtained by plotting rate of charging against voltage. This procedure avoided the calibration of the variable condenser and the troublesome business of adjusting the condenser for each voltage. Fig. 3 shows examples of the curves obtained.

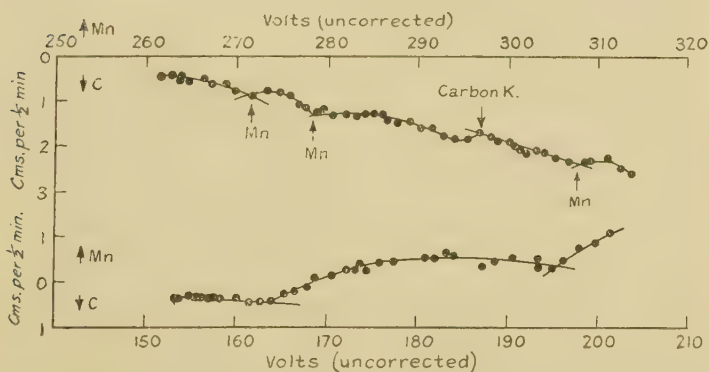
The method has the following advantages:—

(1) It is a null method, and allows the thermionic current to be raised to a high value. This affords greater sensitiveness in the determination of the deviations from the initial value of $\frac{i_{p_2}}{i_{p_1}}$, and hence allows the critical potentials to be observed the more readily.

(2) As anticipated from the analysis, the deviations from the balance position are never very great, and therefore it is possible to take long curves without resetting the condenser.

(3) Equation 2 shows that the balance-point is unaffected by changes in thermionic current. (This is probably only true for small changes of i_t , for large changes would probably cause changes in A & B.) The deviations from the balance-point (measured by the deflexions of the electrometer) should be proportional to the thermionic current, but since these deviations are small it is unnecessary to correct them for the slow gradual changes in i_t . Thermionic current-readings were, however, taken from time to time during the curves.

Fig. 3.



(4) We are left with only two instruments to read—the electrometer, and the standard potentiometer with which the voltage was measured.

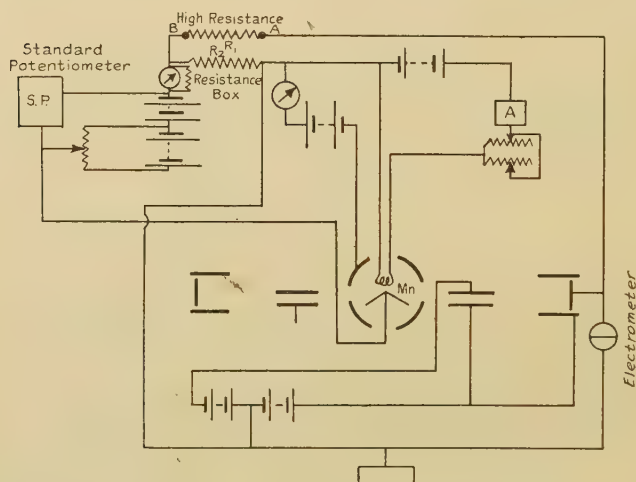
(5) This method was primarily designed to look for and measure the difference between the critical potentials of an element and its compounds. In this case one target would be made of the element and the other of the compound, the critical potentials of each could be obtained on the same curve, and small differences of voltage between the discontinuities could be measured with greater accuracy than if the two targets were examined separately.

The method has a number of disadvantages. It is necessary to know the critical potentials of one of the targets. Carbon was used as the standard target in this

experiment, as one would only expect to get the K discontinuity occurring in the range under examination, and this had been verified by a number of experimenters, who had determined the voltage of the discontinuity. During the course of our experiments, however, a letter from Richardson and Andrewes to 'Nature' announced the discovery of a large number of discontinuities whose position depended on the crystalline state of the carbon.

It is difficult, from the curves obtained by this method, to distinguish between manganese discontinuities and carbon discontinuities. For this reason manganese was subsequently examined by a steady deflexion method which

Fig. 4.



did not involve the use of a carbon target. The steady deflexion experiments indicate that, with the exception of carbon K, practically all the discontinuities obtained by the first method can be obtained from the manganese face of the anticathode. (The exceptions are 132, 248.5, 309.2, and 339.2. The first of these was, however, obtained for Mn by Andrewes, Davies, and Horton.)

The first method also involves, in an aggravated form, the difficulties encountered in using a timing method with an electrometer. If the method is to be sensitive a heavy charge must be allowed to collect on the pairs of quadrants, and leakages are therefore accentuated.

Fig. 4 shows the electrical connexions of the second

method. R_1 is a high resistance constructed by depositing lampblack on a silica rod. R_2 is a resistance-box. The tube used for the first method was again employed, but we now only made use of the photo-electric cell exposed to the manganese radiation. The photo-electric current from this cell flowed through R_1 , so that in the steady state the p.d. between A and B would be $i_{p_1} \cdot R_1$. The thermionic current flows through R_2 , and therefore the potential of A (measured by the electrometer) with respect to earth is $i_{p_2} \cdot R_1 - i_t \cdot R_2$. If this is adjusted to zero by means of the resistance-box R_2 , we have, $VNB i_t \cdot R_1 = i_t \cdot R_2$.

As in the first method the balance-point is independent of the thermionic current. Again it was not considered convenient to adjust R_2 for zero electrometer deflexion at each voltage, and, instead, the value of R_2 was kept fixed during the taking of a set of readings, and the reading of the electrometer taken. This gave a measure of the quantity $i_t \cdot R_1 \cdot \Delta(VN)$, where $\Delta(VN)$ is the change in VN from its value at the balance-point. Readings of i_t were taken, but it was not deemed necessary to divide the electrometer readings, but to leave i_t in the expression as a constant unless the readings of it showed it to vary in such a way as to cause a discontinuity in the electrometer reading—voltage curves. It was deemed wise to abandon such discontinuities. Fig. 5 shows some of the curves obtained by this method.

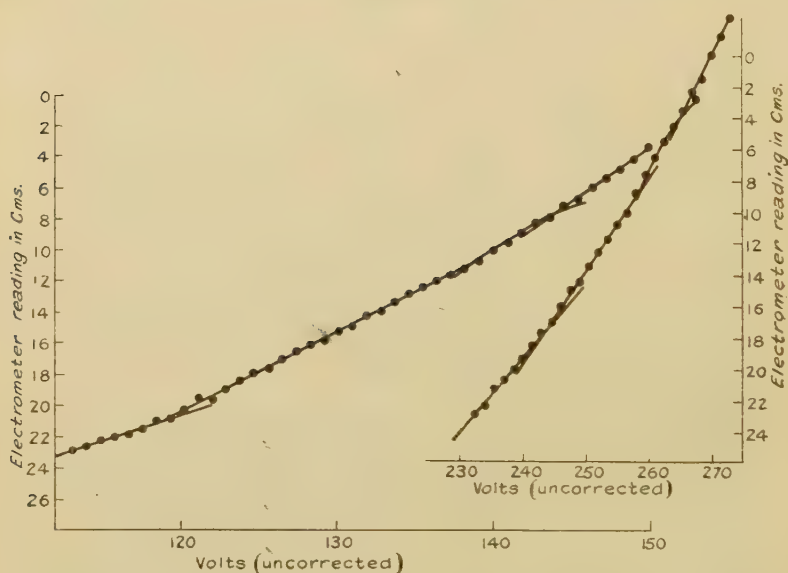
The results obtained by the two methods are shown in Table I. It was feared that the positions of the discontinuities obtained by the second method might be affected by the time-lag in the high resistance. Some curves were taken with increasing voltage and some with decreasing, and it was thought that it might be preferable to take a mean of the average value of a discontinuity on curves of ascending voltage and of the average on descending voltage. For no critical potential, however, did this value differ by more than half a volt from the mean of all the values for the critical potential. We have therefore adhered to the usual method of taking the mean.

Do series similar to those found * for iron, nickel, cobalt, and copper also apply to the results obtained for manganese? For each of these four elements four critical potential series were found of the form $A - b/n^2$, the four series having different values of A , but the same value of b .

* Richardson and Chalklin, Proc. Roy. Soc. A, cxxi. p. 233 (1928).

It was therefore concluded that for each of the elements there were four initial levels which we called X_0 , X_1 , X_2 , and X_3 , from which transitions took place to the same series of final levels represented by b/n^2 . Whether or not the X levels are to be identified with the M levels is at present uncertain. For each of these elements critical potentials occur which appear to be due to transitions from the $L_{II, III}$ level to X levels, and, making use of the combination principle, the $L_{II, III}$ level was calculated. A Moseley diagram of the $L_{II, III}$ level thus obtained for these elements

Fig. 5.



gives a straight line. An extrapolation gives the $L_{II, III}$ level of Mn to be approximately 740 volts. Thoraeus has found the X-ray emission lines $L_{\alpha_{1,2}}$ and L_{β_1} for Mn to occur at 19.39 Å and 19.04 Å respectively. These values are equivalent to 637 and 648 electron volts. For the four elements mentioned the voltages corresponding to these lines were roughly equal to $L_{II, III} - X_3$. If this identification is made for manganese we find $X_3 = 740 - 640$ (approx.) = 100 volts (approx.). It thus appears that the X_3 level is in roughly the same position as for iron, cobalt, nickel, and copper, and that an $X_3 \rightarrow b/n^2$ series will be

outside the range of our present experiments, which did not go below 110 volts.

A knowledge of the wave-lengths of the L_β and L_γ lines would, in a similar way, enable a prediction of the X_1 level, but, unfortunately, the writer has been unable to discover any measurements of these lines.

TABLE I.

Method 1.	Method 2.	Weighted mean.	Andrewes, Davies, and Horton †.
Volts.	Volts.	Volts.	Volts.
—	—	—	49
—	—	—	73
—	—	—	88
—	—	—	105
—	—	—	113
122.1	121.0	121.7	117
132.0	—	132.0	134
—	141.3	141.3	—
145.4	146.8	145.9	—
—	159.8	159.8	157
166.6	168.4	167.9	—
181.9	181.1	181.2	179
193.7	194.5	194.2	189
201.0*	200.4	200.5	—
—	211.5	211.5	—
—	218.2	218.2	—
224.9 *	224.4	224.6 ?	—
239.0	241.3 ?	239.7	—
248.5	—	248.5	—
259.9	259.7	259.8	—
—	265.6	265.6 ?	—
273.6	273.7	273.6	—
284.4	285.3 *	284.5	—
297.9(carbon K ?)	298.8	298.8	—
309.2	—	309.2 ?	—
315.9 *	315.1	315.4	—
—	323.4	323.4 ?	—
—	332.2	332.2 ?	—
339.2	—	339.2 ?	—
362.2 *	361.8	361.9	—
368.1 *	367.8	367.9	—
379.4	378.1	378.7	—
400.8	403.2	401.5	—
412.0 *	411.9 *	412.0	—

* Only obtained on one occasion.

† Proc. Roy. Soc. A, cxvii. p. 649 (1928).

Two series given in Tables II. and III. have, however, been obtained, and appear to be the X_1 and X_0 series. They employ the value 2357 for " b ," as did also the series

of cobalt and nickel (copper also had roughly the same value of b).

The suggested series appears to give only a fair representation of the experimental results. In giving the observed value 146.8 we have neglected the results obtained for this discontinuity by Method I., in which the effect at 141.3 volts was not resolved, and in which, therefore, an effect at 146.8 might be expected to be obtained too low. Even so, the discrepancy between the observed value 146.8 obtained by Method 2 and the predicted value 149.0 is rather large. Again, the experimental values 173.8 and 179.4, which have been taken to correspond to the series values for $n=10$ and $n=11$, were only obtained once, and do not therefore appear in our listed values in Table I.*

TABLE II.

$X_1=197.3$ volts.		
n .	$X_1 - \frac{b}{n^2}$.	Observed.
4	50 volts.	49 volts (A, D, and H).
5	103 "	105 " (A, D, and H).
6	131.8 "	132.0 "
7	149.0 "	146.8 " (value from Method 2).
8	160.8 "	159.8 "
9	168.2 "	167.9 "
10	173.7 "	173.8 " (only observed once).
11	177.8 "	179.4 " (only observed once).
12	180.9 "	181.2 "

(The two A, D, and H values used were beyond the range of the present experiments.)

On the other hand, it would be reasonable to expect that for such large values of n the critical potentials would be weak. The readiness with which the 181.1 break was obtained in Method 2 was probably due to its being made up of more than one unresolved effect.

The suggested series has, however, a number of virtues. There has been no necessity to change the constant b from the value used for the series of Co, Ni, and Cu. Secondly, the series accounts for all the discontinuities which we have obtained in this region except those at 141.3 and 121.9 volts, and of these the 141.3 break is accounted for below.

There appears to be evidence in favour of another series with the same value of b and with a limit approximately

* Andrewes, Davies, and Horton have a critical potential at 179 volts.

the same as that of the X_0 series for iron. This is shown in Table III.

This series seems to be quite satisfactory apart from the value for $n=8$, in which the observed critical potential is 3 volts from the predicted value. Again, the series has accounted, with some completeness, for the critical potentials found in the region concerned, and it will be noticed that, with the exception of the 121.7 effect and three breaks between 200 and 220 volts, the two series together account for all the critical potentials obtained by the writer below 280 volts.

The critical potential series scheme does not in its present form account for the discontinuities found for manganese above 280 volts, and for iron, cobalt, nickel, and

TABLE III.

$X_0=288.3$ volts.		
n .	$X_0 - \frac{b}{n^2}$.	Observed.
4	141.1 volts.	141.3 volts.
5	194.0 "	194.2 "
6	224.8 "	224.6 ? "
7	240.2 "	239.7 "
8	251.5 "	248.5 "
9	259.2 "	259.8 "
10	264.7 "	265.6 ? "
11	268.7 "	—
12	271.8 "	
13	274.3 "	273.6 "

copper there were unpredicted effects in this region. It is therefore clear that, if it is to be comprehensive, the series scheme will require extension. The data at present available do not, however, justify such an extension.

In conclusion, the writer wishes to express his gratitude to Professor O. W. Richardson for his advice and interest in the experiments; to Professor S. R. Milner, in whose department this work has been carried out, for his interest and encouragement; and he is indebted to his wife (L. P. Davies), who has rendered very valuable assistance in the carrying out of the experiments.

Thanks are due to the Government Grant Committee of the Royal Society for a grant by means of which apparatus was purchased.

LXXIX. *The Effective Temperature of a Warmed Room.*

By A. F. DUFTON, M.A., D.I.C.*

[Plate XI.]

1. **E**XPERIENCE shows that when the walls of a room are cold a higher air-temperature is required for comfort than when the walls are warm. In a comfortably warmed room a sedentary man loses by radiation and convection some 17·5 B.Th.U. per square foot of effective surface per hour, and if normal clothing be worn, the average temperature of the surface from which this heat is lost to the room is about 75° F. Under such conditions, as has been pointed out by Dr. Hill, of the National Institute for Medical Research, changes in the humidity are immaterial so far as heat losses are concerned †.

Pending a more precise physiological standard of thermal comfort, a provisional standard has been based upon this rate of loss of heat, according to which a room is postulated to be comfortably warmed where a sizable black body at 75° F. loses heat at the rate of 17·5 B.Th.U. per sq. ft. per hour ‡.

The temperature of an environment with air and walls at different degrees is not easily specified. From the point of view of comfort it is the rate at which heat is lost from the body which is important. The effective temperature of an environment may therefore be defined as that temperature of a uniform enclosure in which, in still air, a sizable black body at 75° F. would lose heat at the same rate as in the environment.

2. An instrument has been constructed to record the effective temperature in a room. A thermostatic device tends to maintain at 75° F. the surface of the instrument, a black-painted hollow copper cylinder. The cylinder, which sits on a 28 in. wooden stool, is 22 in. high and 7½ in. in diameter, a replica of that used as an automaton § for regulating the heating of a room. It is heated electrically and the power supplied, which is controlled by the thermostat, is recorded. The power record is scaled to give the

* Communicated by the Author.

† Medical Research Committee, Special Report, no. 32, p. 100.

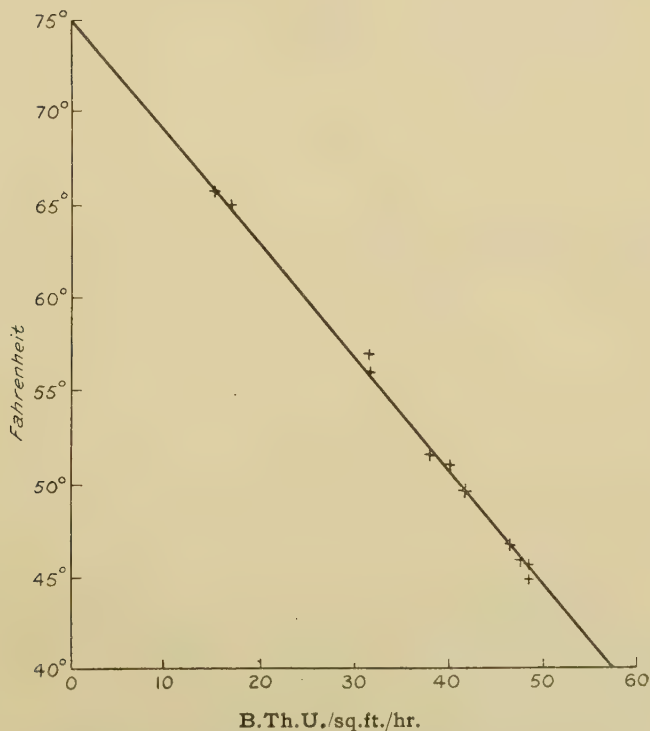
‡ Journal of Scientific Instruments, vi. p. 249 (1929).

§ "The Eupatheostat," Journal of Scientific Instruments, *loc. cit.*

rate at which the cylinder loses heat or, more conveniently, in degrees of effective temperature.

The scale of effective temperature was determined experimentally by recording the heat loss in still air in a room with air and walls at the same temperature. Corresponding values are plotted in fig. 1. An effective temperature of 64.3°F . corresponds with a heat loss of 17.5

Fig. 1.



Relation between effective temperature and the heat loss from a body at 75°F .

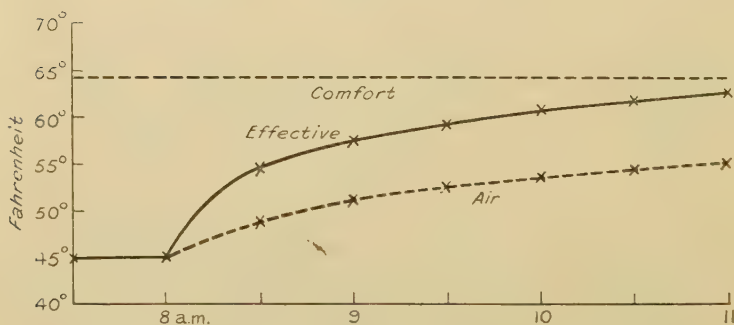
B.Th.U. per sq. ft. per hour, the provisional standard of thermal comfort.

The instrument, which it is proposed to call the Eupatheoscope, in contradistinction to the Eupatheostat, is required for the investigation of the influence of the fabric of the walls upon the rate of warming of a room.

3. Some rooms are not readily warmed and it has been demonstrated theoretically * that, with double the rate of heating which serves to maintain warmth, the time taken to warm the surface of a 9-inch brick wall is six hours, while for a 1-inch wall of wood affording the same insulation the time is ten minutes.

Fig. 2 is a record of the warming of a small furnished room with walls of 9-inch brick plastered internally. It shows not only the slow rise of the temperature of the air but also that, even in the radiant heat 8 ft. from a gas fire burning 0.2 therm per hour, a comfortable warmth was not attained in three hours.

Fig. 2.



The warming of a room.

4. For measuring the effective temperature of a room a special kata-thermometer has also been devised. To ensure that the surface is at the same temperature as the thermometric liquid, the bulb is made of copper with a very thin lining of glass (0.4 mm.) and the thermometer is filled with mercury. The thermometer is allowed to cool from $75\frac{1}{2}^{\circ}$ F. to $74\frac{1}{2}^{\circ}$ F.—in a comfortably warmed room this takes one minute—and the stop-watch used for timing is graduated in degrees of effective temperature (Pl. XI.). The thermometer is readily warmed with the hands.

The kata-thermometer was compared with a eupatheoscope in the same environment. Corresponding readings are shown in the Table (p. 861).

* Phil. Mag. iv. p. 888 (1927).

It was anticipated that some allowance would have to be made for the excessive convection loss of the thermometer, due to its small dimensions. To enable this to be effected the cooling in the same environment of a similar thermometer with a silvered bulb was observed. The experiments

Air Temperature.	Effective Temperature.	
	Eupatheoscope.	Kata-thermometer.
46° F.	46·1° F.	45·7° F.
50	50·0	50·2
53	56·6	57·1
58	33·9	63·7
61	65·8	65·6
62	67·0	66·5
65	65·0	65·2

showed, however, that the auxiliary thermometer affords no advantage and that the cooling of the black thermometer gives a sufficiently accurate measure of the effective temperature.

LXXX. *Notices respecting New Books.*

A Comprehensive Treatment on Inorganic and Theoretical Chemistry.
By J. W. MELLOR, D.Sc. Vol. IX. As, Sb, Bi, V, Cb, Ta.
[Pp. xiv+967.] (London: Longmans, Green & Co., Ltd.,
1929. Price 63s. net.)

THE ninth of the thirteen volumes which will comprise Dr. Mellor's 'Comprehensive Treatise' is devoted to the trivalent and quinquevalent elements, arsenic, antimony, bismuth, vanadium, columbium, and tantalum. It follows the same general lines as the preceding volumes. For each element an account is given of its history, occurrence, methods of extraction, physical and chemical properties, its uses, its atomic weight, and valency. Then follow sections devoted to the various compounds of the element. An important feature of the work is the comprehensive list of references to original sources; an examination of these indicates that the literature up to and including the year 1927 has been incorporated in the present volume.

The elements dealt with in this volume have several features of interest, as poisons, as possessing allotropic modifications, as forming colloidal solutions, and as constituents of metallic alloys. These properties are all fully dealt with.

The volume, along with the other volumes of the series, will be found invaluable for reference purposes, not only by chemists, but also by physicists and other scientific workers.

Elementary Applications of Statistical Method. By H. BANISTER, B.Sc., Ph.D. [Pp. vi+58.] (London: Blackie & Son, Ltd., 1929. Price 3s. 6d. net.)

THOSE who have to deal with statistical data and who possess no training in mathematics or statistics will find this small volume a suitable introduction to statistical methods. For such persons it can be followed with advantage by Fisher's 'Statistical Methods for Research Workers.' Such subjects as the tabulation of data, frequency distribution, goodness of fit, measures of dispersion, the significance of the mean and of the difference between the means of two samples and correlation, are dealt with in a very brief and elementary manner, and illustrated by simple examples. Probability tables and tables of goodness of fit are given in Appendices in a graphical form. Four figure tables of logarithms and anti-logarithms are also included; these might well have been omitted, being probably accessible in one form or another to all who will use this book.

The Elementary Differential Geometry of Plane Curves. By R. H. FOWLER, M.A., F.R.S. (Cambridge Tracts in Mathematics and Mathematical Physics, No. 20.) [Second Edition. Pp. ix +105.] (Cambridge: at the University Press, 1929. Price 6s. net.)

THE value of this work lies in the fact that a connected account of the elementary differential properties and geometry of plane curves was not previously available in the English language. The author does not claim that the matter is in any sense new nor that the treatment is novel. The treatment is, however, rigorous and connected, and the tract will be welcomed by those who do not possess Goursat's 'Cours d'Analyse' or some similar work.

The first edition appeared in 1920. The second edition is unaltered except for the correction of various mistakes. The author states in the preface to this edition that "I have not been in any way concerned with this subject since this tract was first published." It is to be regretted that Prof. E. H. Neville's revised theory of envelopes has not been incorporated, though the nature and scope of this is clearly explained in the preface. To have incorporated this would have necessitated a somewhat extensive revision of the work, for which presumably the author could not find time. On the principle that half a loaf is better than no bread, we must be thankful that the publishers have not permitted the tract to go out of print, and that this well-written account of the differential geometry of plane curves is still obtainable.

LXXXI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 672.]

December 4th, 1929.—Prof. J. W. Gregory, L.L.D., D.Sc.,
F.R.S., President, in the Chair.

THE following communication was read:—

‘Foliation in its Relation to Folding in the Mona Complex at Rhoscolyn (Anglesey).’ By Edward Greenly, D.Sc., V.P.G.S.

Further studies on the major anticline of Rhoscolyn have thrown much light on successive stages of the metamorphism.

The major, minor, and minimum foldings (with their thrustings) have each given rise to a foliation; that produced by the major folding being, on the nearly horizontal core of the great anticline, conspicuously transverse to the bedding of the massive grits of the South Stack Series. Yet it is thrown into isoclines by the minor folding, which is therefore subsequent to it. Where the cross-foliation of the major folding has been isoclinally folded, the foliation of the minimum folding runs right up to it at any angle without being itself folded in the least, whence it follows that the minimum is later than the minor structure. Thus the three foliations (major, minor, and minimum) developed in chronological order.

Thrusts often truncate the minor isoclines, and on decapitated anticlines where the beds are steep the beds above and below the thrust have been made to interdigitate. Sometimes this is carried so far as to drive long wedges of thin grits in between the laminae of the major cross-foliation. In this manner the structures usually found at a thrust-plane have often been completely obliterated, even when the thrust is considerable.

The relations of major to minor folding furnish an explanation of the fact that the major cross-foliation, unlike a slaty cleavage, fails to traverse the pelitic beds. The foliation of the plutonic intrusions, and the tremolite-schists, are products of the major movements.

In ‘The Geology of Anglesey’ the principal metamorphism was ascribed to the major and subsequent movements. Re-examination has shown, on the contrary, that this metamorphism is independent of, and older than, all three. Its foliation is developed along innumerable thrusts, but these are at angles so acute to the bedding that, especially when thrown into rapid isoclines, they easily escape notice. This is the true explanation of ‘monoplastic schists.’

The view now abandoned was based upon the aureoles of the basic intrusions, but a fresh study has revealed that their evidence gives decisive confirmation of the view now adopted. They are frequently cut by thrusts of the major series, but are never affected by the principal metamorphism. There are several lines of evidence, perhaps the most striking being the fact that the thermal minerals of the aureoles crystallize across and obliterate the planes of the

principal metamorphism, which is, therefore, anterior to the intrusions and thus to the major folding.

This early foliation is really the regional metamorphism. But the thrusting to which it is due, unlike those of the three later series, can be referred to no visible folding. Accordingly, its disentanglement goes to confirm the hypothesis that recumbent folding exists, and is the dominant structure of the Mona Complex.

These studies, carried out only on a single tectonic horizon, greatly extend the chronology of the metamorphism of the Mona Complex.

December 18th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc.,
F.R.S., President, in the Chair.

The following communication was read:—

‘The Geology of the Shiant Isles’. By Frederick Walker, M.A.,
Ph.D., D.Sc.

The Shiant Isles form a small uninhabited archipelago in the North Minch, some 5 miles east of the Park district of Lewis. The group is made up almost entirely of crinanite sills separated by relatively thin argillaceous strata which have undergone considerable contact-alteration, but the fossil content of which (ammonites, belemnites, and one species of *Inoceramus*) assigns them to a low position in the Upper Lias. The two largest islands are each over a mile in length, and are joined by a shingle-beach. Their principal feature is a crinanite sill at least 500 feet thick, with a picrite base. The transition between the crinanite and the picrite is gradual, and the ultrabasic rock is considered to have accumulated by the gravitational settling of olivine-crystals, this hypothesis being borne out by a series of chemical analyses, modes, and specific gravities. Numerous veins of teschenitic and syenitic composition pierce the picrite, and probably represent the expulsion of residual magma at various stages during crystallization.

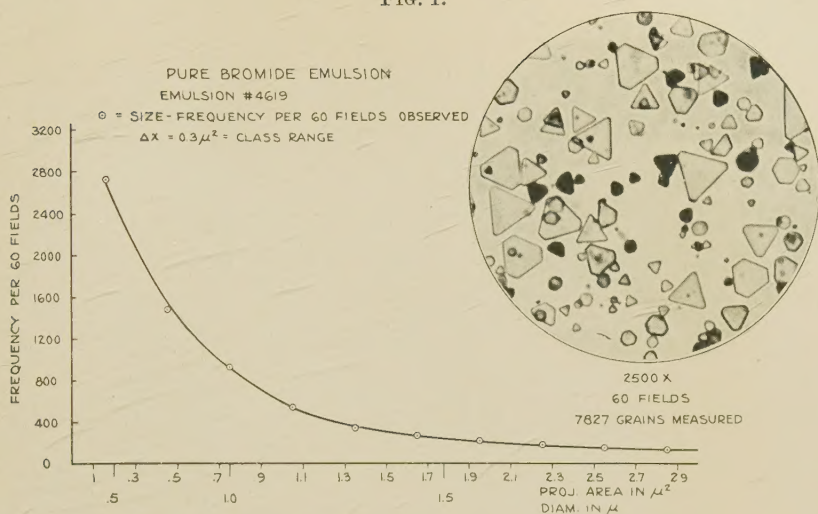
A third large island lies about a mile to the east of the other two, and is also to a great extent made up of a single thick sill of crinanite. East of this island, however, the crinanite passes gradually into syenite, towards the centre of the sill, the thickness of the alkaline rock being at least 60 feet. The syenite carries abundant analcite and occasional nepheline, but otherwise resembles closely the rock of Gamhnach Mor in Mull. It is riddled by veins of still more alkaline material, and cut by horizontal sheets of olivine-basalt which are chilled against it. The alkaline centre of the sill is thought to have originated through auto-intrusion caused by pressure on the crystal-mesh of the crinanite. Similar syenitic bands occur in the crinanite of the smaller islands.

The age of the igneous activity is almost certainly Tertiary, and is probably the same as that of the Trotternish sills in Skye.

Although glacial striæ are not seen on the islands, their general aspect indicates a flow of ice from south to north during the Glacial Period.

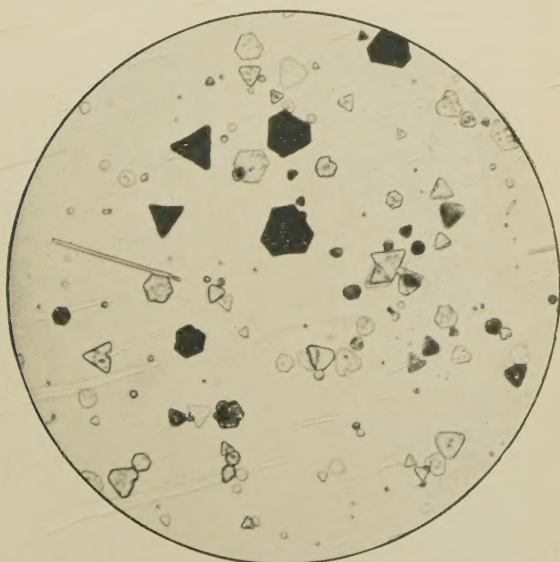
[The Editors do not hold themselves responsible for the
views expressed by their correspondents.]

FIG. 1.

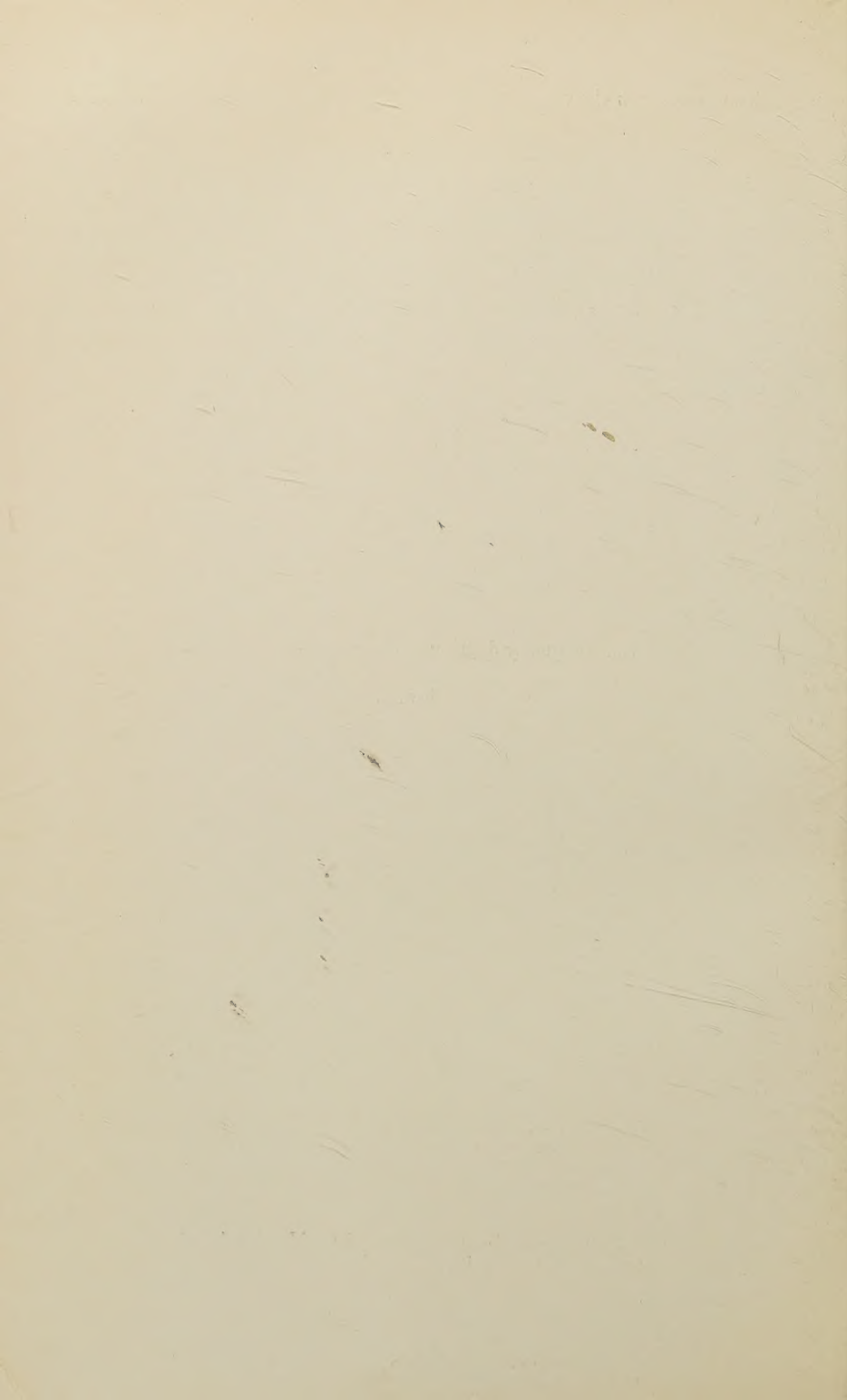


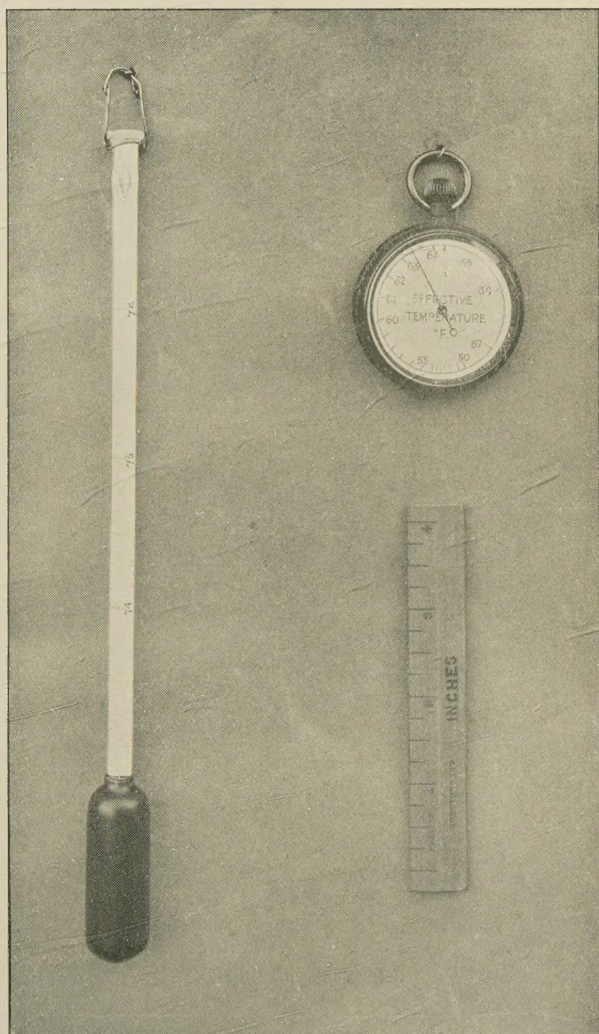
Size-frequency distribution of pure silver bromide.

FIG. 2.



X-ray exposure on pure silver bromide, developed with hydroquinone.





Effective Temperature Thermometer.

